A Synopsis of

The Electronic Structure of Some Second Row Elements in High Oxidation States.

by

B. C. Webster B.A.

A thesis submitted for
The Degree of Doctor of Philosophy
in the University of Glasgow.

June 1967.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

Synopsis

The core of the studies presented here is the calculation of numerical self consistent field wave functions for the second row elements Si, P, S, Cl and Ar in excited configurations which involve the 3d orbital. In many discussions of the bonding in molecules which contain these elements as their central atoms, it si maintained that the 3d orbital may have an important role. To take a classic example, on the basis of the concept of hybridisation Pauling has interpreted the bonding in sulphur hexafluoride in terms of the formation by the sulphur atom of sp^3d^2 hybrids. Later it was observed that the maximum in the 3d wave function, if taken to be of a Slater type, lay well beyond the S - F internuclear distance. On further investigation, the use of the Slater 3d orbital in this context was judged to be quite acceptable and an elaborate theory was developed to bring the 3d orbital into a form suitable for bonding.

This situation persisted to the time this work was commenced, though on occasions it had been suggested that perhaps the Slater 3d orbital is not a suitable representation for the 3d wave

function of $S(sp^3d^2)$.

In the opening chapter of this thesis, the course of such disputations is placed in perspective against a background of the chemical thought prevailing at the period and the problems involved are formulated. For a satisfying solution it is found to be necessary to perform a series of self consistent field calculations, and to investigate more fully the concept of the valence state. Chapter II treats in detail the theory of the self consistent field and the manner in which atomic calculations are performed. This is followed by a study of the valence state concept utilising the theory of the symmetric permutation group. Some very interesting results are obtained.

The subsequent two chapters are concerned with the shape and energy of the valence orbitals possessed by the elements mentioned when in high oxidation states. It is discovered that many affirmations which have been made on the subject of the 3d orbital are unfounded and indeed quite erroneous. This is rather surprising in view of the admirable investigations performed on this topic by Craig and his collaborators during the

past decade. Their theories are therefore closely examined in Chapter VI and discrepancies explained.

On reaching the closing pages it is possible to suggest in what manner a '3d orbital' might assume a role in the bonding of the second row elements under review. Finally a plea is made that the concept of hybridisation must now give way to the concept of polarisation if the development of chemical thought is not to be inhibited.

The Electronic Structure of Some Second Row Elements in High Oxidation States.

by

B. C. Webster B.A.

A thesis submitted for
The Degree of Doctor of Philosophy
in the University of Glasgow.

June 1967.

Acknowledgments

The studies presented in this thesis were performed whilst I was a Research Assistant in Theoretical Chemistry at the University of Glasgow. This post was held in the department of Professor D.W.J. Cruickshank to whom I am extremely grateful for introducing me to this field of study and for his continual interest in the work as it progressed over a period of four years.

I should also like to express my gratitude to Dr. David Mayers of the Oxford Computing Laboratory for advice on the solution of atomic self consistent field equations and to Dr.Graham Doggett for many helpful discussions. Finally my thanks are due to my wife,Mary,for typing the manuscript.

CONTENTS

Chapter VI. Page

Units

Except where is otherwise stated all distances quoted in the text are in Angstroms ($1\ \text{Å} = 10^{-8}$cm) and all energies are in electron volts.
(1 e.v. $= 8106\ \text{cm}^{-1}$).

CHAPTER I

SOME PROBLEMS ARE PLACED IN PERSPECTIVE

> It must not be supposed that atoms of every sort can be linked in every variety of combination.
>
> Lucretius 55 B.C.

Introduction

The manner in which the elements combine is the essence of chemistry. For this reason it has become a perennial problem, each generation having of necessity to formulate some model for chemical combination. Naturally, these are framed by the concepts prevalent at a particular period. As the concepts evolve or are found to be inadequate, the models either become richer in content or pass into disuse. Often, prior to disuse, attempts are made to preserve a model by the addition of ever alien features. It is the relative rate of these processes which governs the progress of the science.

This present study on the theory of chemical

binding advances no new concepts,but examines some, which of recent times have become rooted in our thought. It is principally concerned with the elements which lie towards the end of the second short period in Mendeleeff's classification. These are silicon Si, phosphorus P, sulphur S, chlorine Cl, and argon Ar. They do,indeed,form a touchstone upon which a number of theories have faltered. Let us call some of these to mind and in so doing trace the theory of valence up to 1926.

Pre Wave Mechanical Theories

Berzelius' duality theory proposed in 1812 captivated the chemical imagination for a quarter of a century[1]. This theory,incorporating the earlier ideas of Davy and Avogadro,is based on two premises; every atom possesses two electrical poles of opposite sign and unequal strength,and oxygen is the most electronegative element. Magnesium sulphate is soregarded as being formed from two oxides,one electropositive,the basic oxide MgO,and one electronegative,the acidic oxide SO_3.

$Mg^{+} + O^{-} \rightarrow MgO^{+}$

$S + 3O^{-} \rightarrow SO_3^{-}$

$MgO^{+} + SO_3^{-} \rightarrow MgO.SO_3$

There remains a slight residual charge which is neutralised on addition of water to produce the heptahydrate $[MgO.SO_3]\ 7H_2O$.

Faraday's observations that equal quantities of electricity are associated with the equivalent weights of the elements discredited Berzelius' first postulate. The increase in knowledge of the properties of chlorine cast doubt upon the second. When Dumas discovered that chlorine could replace hydrogen in organic molecules without a gross alteration in their chemical behaviour, dualism was soon discarded. However the idea of attributing molecular binding to an electrical interaction had been planted.

The picturesque theory of types now became the vogue. This was passing into a highly decorative form when Frankland published his paper on 'A New Series of Organic Compounds containing Metals' [2]. This work, dated 1852, marks the beginning of a theory of valence. Franklands achievment lies in his recognition that in the formation of a molecule

'no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms'. Phosphorus, for example, is attributed a combining capacity of three or five. It appears doubtful as to whether Frankland himself realised the far reaching import of this remark for he now proceeds to effect a marriage of the duality theory and the theory of types.

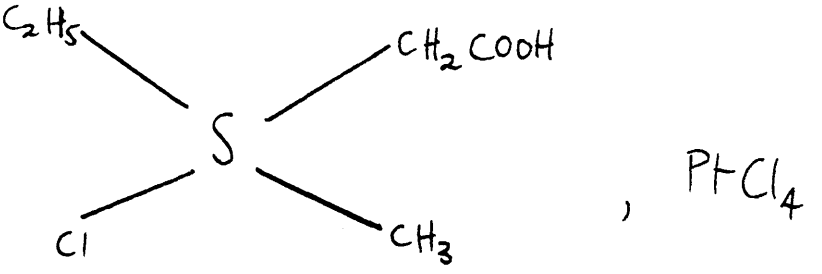
The term valency was introduced in 1868 [3], by which time Kekule and independantly Cannizzaro had crystallised the content of Frankland's paper into a viable theory [4]. Kekule, however, maintained that the valency of an element is a fixed property. In consequence he had to resuscitate Berzelius' ideas to explain the existence of compounds in which the valence number is exceeded. Phosphorus pentachloride is so formulated as being a molecular compound $PCl_3.Cl_2$ which appeared reasonable for on thermal decomposition chlorine is liberated.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

After Thorpes preparation of the thermally stable,

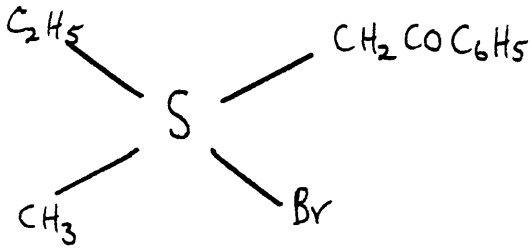
gaseous pentaflouride PF_5 in 1877, it became clear that a variable valency is indeed exhibited by phosphorus, and is likely to be common to other elements.

Kekule's influence persisted. Pope and Peachy write in 1900 'since the discovery of the sulphonium compounds by Oefele in 1864, attempts too numerous to be recapitulated here have been made to ascertain whether the sulphur atom is capable of combining with four separate univalent groups or whether derivatives of apparently quadrivalent sulphur are merely molecular, as distinct from atomic compounds. These attempts have up to the present yielded negative or ambiguous results.' They continue by reporting the preparation of the optically active compound d-methyl-ethyl-thetine-platinichloride,

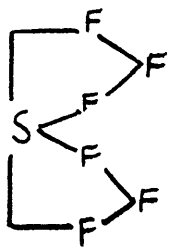


demonstrating 'that in compounds of the type SX_4

the sulphur atom is truely quadrivalent and that the four groups attached to it are, as in the case of carbon, situated at the apices of a tetrahedron, the the interior of which is occupied by the sulphur atom [5]. Smiles in deference to Pope and Peachy refrained from publishing his preparation of the compound



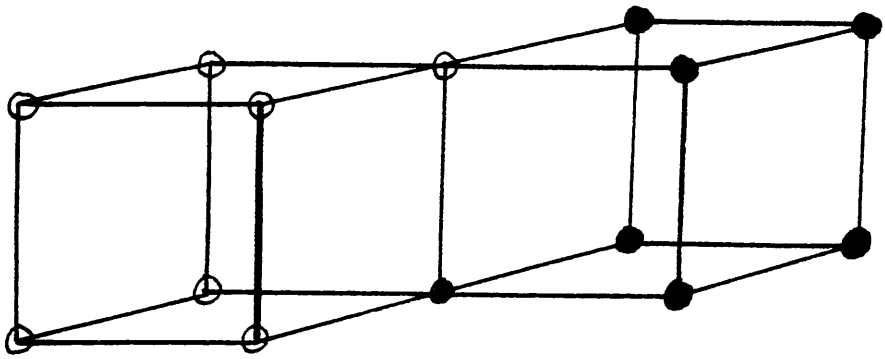
until later that year [6]. Optically active compounds of silicon [7] and phosphorus [8] were subsequently prepared. The extent to which a theory of valence had been assimilated at the beginning of this century is epitomised by de Forcrand's formula for sulphur hexafluoride, SF_6 [9].



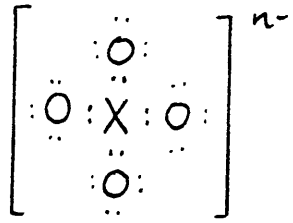
Elsewhere the subject seethed with expectancy. Thomson had identified the electron. In 1904 he

suggested that chemical combination might be due to the transfer of electrons from one atom to another and to the static forces which must result.[10] Simultaneously Abegg proposed his rule of principal and contravalences [11]. By this, each element is considered to exert a normal valency, which is positive for metals, negative for nonmetals, and less frequently a contravalency, such that their sum is equal to eight. Sulphur is normally divalent, as in hydrogen sulphide, but in the hexafluoride exerts a contravalence of +6.

These two suggestions, and particularly that of Abegg, had a profound influence on subsequent chemical thought. The ideas of many were finally synéthesised by Kossel [12] and independantly by Lewis [13] into the well known octet theory. This titular emphasis on the word octet is unfortunate for Lewis's postulate that a covalent bond is formed by a pairing of two electrons, has the deeper significance. Despite shortcomings, the theory became deservedly popular. Its static character is in evidence when one views for example the structure proposed for chlorine.



The seven valence electrons of each atom are disposed at the corners of a cube. By the sharing of an edge the octet is completed and a link formed. The oxyanions of the second row elements $(XO_4)^{n-}$ seemed perfectly adapted to the theory.



$X = Si, P, S, Cl$

$n = 4, 3, 2, 1$

Whilst the nonexistence of FO_4^- could be regarded as an anomaly, the existence of the species $[SiF_6]^{2-}$, PCl_5, SF_6 was clearly an embarassment.

Opinions held in the early twenties may be savoured in the discussion upon the Electronic Theory of valency held by The Faraday Society on July 13th and 14th 1923 in the Department of

Physical Chemistry,Cambridge [14]. Fowler's remarks are apposite. ''The formation of sulphur hexafluoride has been explained by treating it as the fluoride of hexavalent metallic sulphur $^{+++}_{S}$ F_6^-. This view is open to objection on the ground that it has none of the properties of a metallic salt. On the other hand,it is not at all unlike a co-ordinated compound of a metal;and there are obvious analogies between the ions $PtCl_6^{2-}$ and SiF_6^{2-},which would lead to the view that SiF_6^{2-} is a co-ordinated radical and that SF_6 is a co-ordinated compound, [S.6F],like [Mo.6Co]. Is it possible that there is here a shell of 12 electrons - i.e. that the electrons are grouped in the series 2, 8, 12, is spite of the fact the usual series is 2, 8, 8,?

(Ans.) Here again chemistry must take the lead. Physics is at present completely ignorant,but it certainly has as yet no objection whatever to the series 2, 8, 12(shared),with presumably octahedral symmetry for the latter. After all physics demands at a later stage 2, 8, 18, --- with approximately octahedral symmetry in the 18. It is merely a matter of energy considerations(which are as yet beyond us) at what stage the 18 group should be formed. In

the free atom, of course, it does not begin to form till Sc; but there is no reason why it might not occur in this partial form at Si or S in a compound. A co-ordinated compound [O. 6F] would be very repugnant to physical ideas of atomic structure; but not necessarily [S. 6F].''

With the increasing study of molecular structure and reactivity the demands placed upon valency theory were becoming ever more stringent . No longer was it sufficient just to be able to interpret the law of multiple proportions. Interatomic distances between two given atoms were being observed to vary quite markedly in different molecules. Why is one shape for a molecule prefered to another? How is the nonexistence of certain molecules to be explained? Phosphorus pentachloride PCl_5 may be prepared but seemingly not NCl_5 or $AsCl_5$; SF_6 but not SH_6; $HClO_4$ but not HFO_4 or $HBrO_4$; Bohr's atomic theory was quite incapable of providing a basis for dealing with such questions. As wave mechanics developed, the theory of valence acquired a totally new complexion, and these problems now seemed to be within its grasp. Let us continue by

examining some of the solutions offered for molecules whose central atoms are Si, P, S, Cl or Ar. From this series, sulphur is selected for particular mention since it lies at the medial position. Our purpose is to bring the central theme of this study, the role of d orbitals in the bonding of these second row elements, into relief against a background of current theory.

The Concept of Hybridisation

By treating molecular formation as an interaction between suitably prepared atoms, the theory of hybridisation [15] presupposes that the free atom and the atom in the molecule may be regarded as similar species. This theory has become very familiar, since its conception in 1931, indeed so familiar that it is perhaps now taken for granted. Formally, it constructs from a set of atomic orbitals, which are nondirectional with respect to a group of ligands, an equal number of hybrid orbitals which are directed towards the ligands. By an overlap of hybrid orbitals orbitals, which are usually assummed to be singly occupied, of the central atom with orbitals on the ligands, a σ-framework for the molecule is formed. Often, the number of bonds which

are required exceeds the number of orbitals immediately accessible for hybrid formation, when the atom is in its ground state configuration. For example sulphur is hexavalent in SF_6 yet in its ground state only two orbitals are singly occupied, $S(s^2p^4)$ - ^3P. This difficulty is overcome by assumming that during the reaction in which the molecule is formed, the atoms are in excited states. Normally only one excited state is considered, that which may immediately be seen to provide the required number of bonds. Sulphur is so taken as having a configuration $S(sp^3d^2)$ in the hexafluoride. It is further recognised that the electrons occupying the hybrid orbitals possess a random spin, so that it is not permissible to specify the lowest term of the configurations, as being solely involved. Consequently the energy of excitation, refered to as the promotion energy, has appeared as a guage to assess whether molecular formation is likely or otherwise. As such it is quite unsatisfactory; there is no way of determining per se as to whether a promotion energy is too high to permit a reaction to proceed and most opinions in this matter appear to be based on arbitrary judgements. It is evident that in order

to form the most effective hybrid orbitals from a set of atomic orbitals three requirements need to be satisfied. The atomic orbitals should possess

(1) a suitable symmetry

(2) a similar size

(3) a similar energy.

Although it is now taught as a chemical fact that the sulphur atom in SF_6 is sp^3d^2 hybridised, it transpires that no serious attempt has ever been made to discover whether such a representation is at all adequate. It may readily be shown that the 3s, 3p and $3d_{x^2-y^2}$, $3d_{z^2}$ orbitals of sulphur possess adequate symmetry. Under the group O_h, six equivalent hybrid orbitals transform as $A_{1g} + E_g + T_{1u}$ whilst s orbitals transform as A_{1g}, p as T_{1u} and d as $E_g + T_{2g}$, hence $S(sp^3d_{x^2-y^2}\ d_{z^2})$ is acceptable.

Pauling disposes of the second and third requirements by assumming that the differences in the radial portions R(r) of the 3s, 3p, and 3d wave functions are so small that they may be neglected. The hybrid is so constructed from the angular portions $S_{lm}(\theta, \phi)$ of the wave functions. One may recall that the wave function for an electron

moving in a central field is of the form

$$\psi(r, \theta, \phi) = R(r) \cdot S_{lm}(\theta, \phi) \cdot$$

When $l = 2$, $m = \pm 1$, ± 2 or 0 and the d orbital is defined. In their real forms these functions are designated as d_{xz}, d_{yz}, d_{xy}, $d_{x^2 - y^2}$, and d_{z^2} where

$$3d_{xz} = R(r) \cdot (15)^{\frac{1}{2}} \cdot \sin\theta \cos\theta \cos\phi$$

$$3d_{yz} = R(r) \cdot (15)^{\frac{1}{2}} \cdot \sin\theta \cos\theta \sin\phi$$

$$3d_{xy} = R(r) \cdot (15/4)^{\frac{1}{2}} \cdot \sin^2\theta \sin 2\phi$$

$$3d_{x^2 - y^2} = R(r) \cdot (15/4)^{\frac{1}{2}} \cdot \sin^2\theta \cos 2\phi$$

$$3d_{z^2} = R(r) \cdot (5/4)^{\frac{1}{2}} \cdot (3\cos^2\theta - 1)$$

A common factor of $(2\sqrt{\pi})^{-1}$ is omitted. Figure 1 illustrates the angular properties of the 3d orbital whilst in Figure 2 an octahedral hybrid orbital is depicted. This hybrid, pointing in the +z direction, has the form

$$\psi_{+z} = \frac{1}{\sqrt{6}} (s + \sqrt{3}p_z + \sqrt{2}d_{z^2}).$$

The emphasis placed upon the angular portion of the wave function is carried further by Pauling and Sherman in their criterion for bond strength [16]. This assumes that a measure of the strength of a

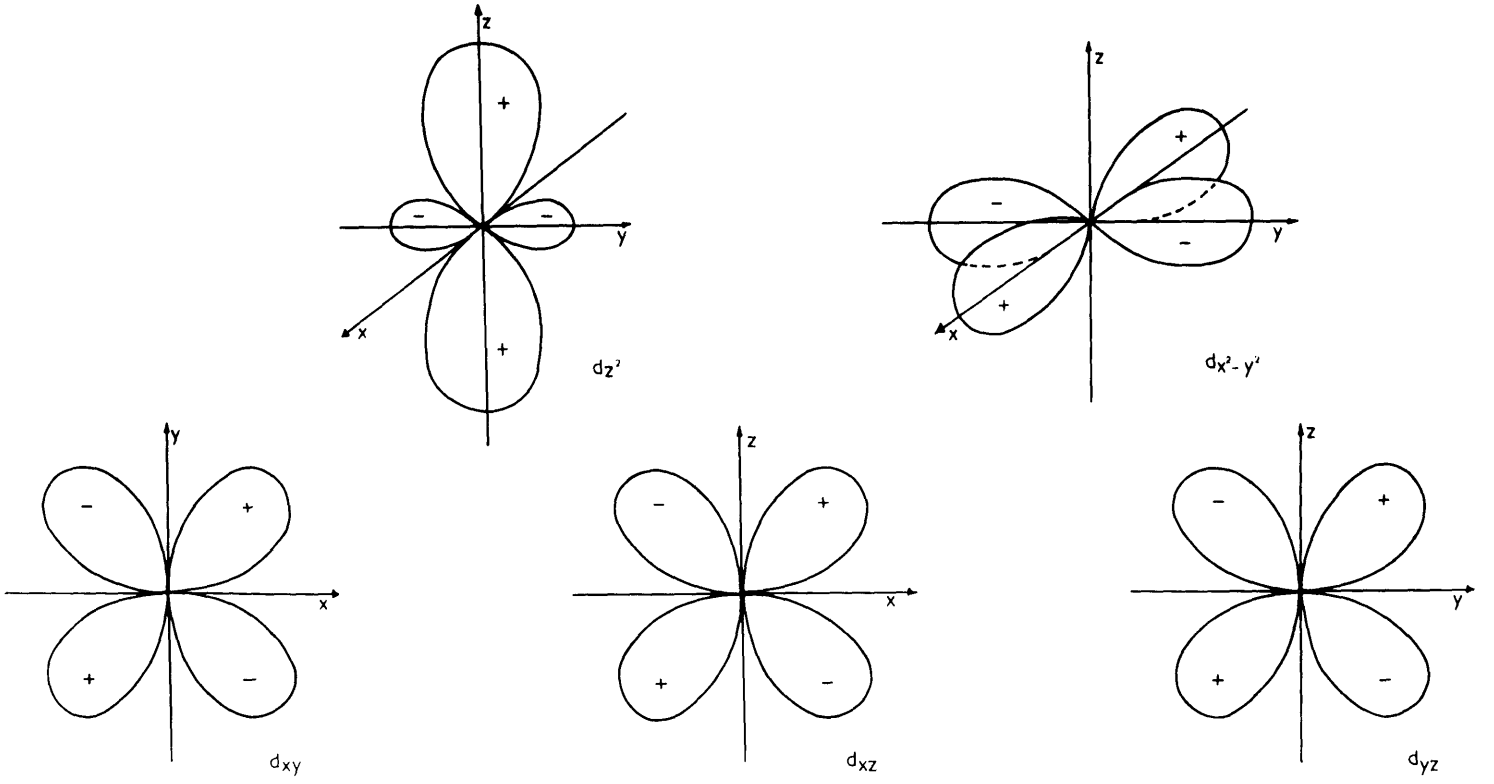


Fig. 1. The magnitude of the angular portions of the 3d wave functions plotted as a function of the polar angle. The + and - refer to the sign of the wave function.

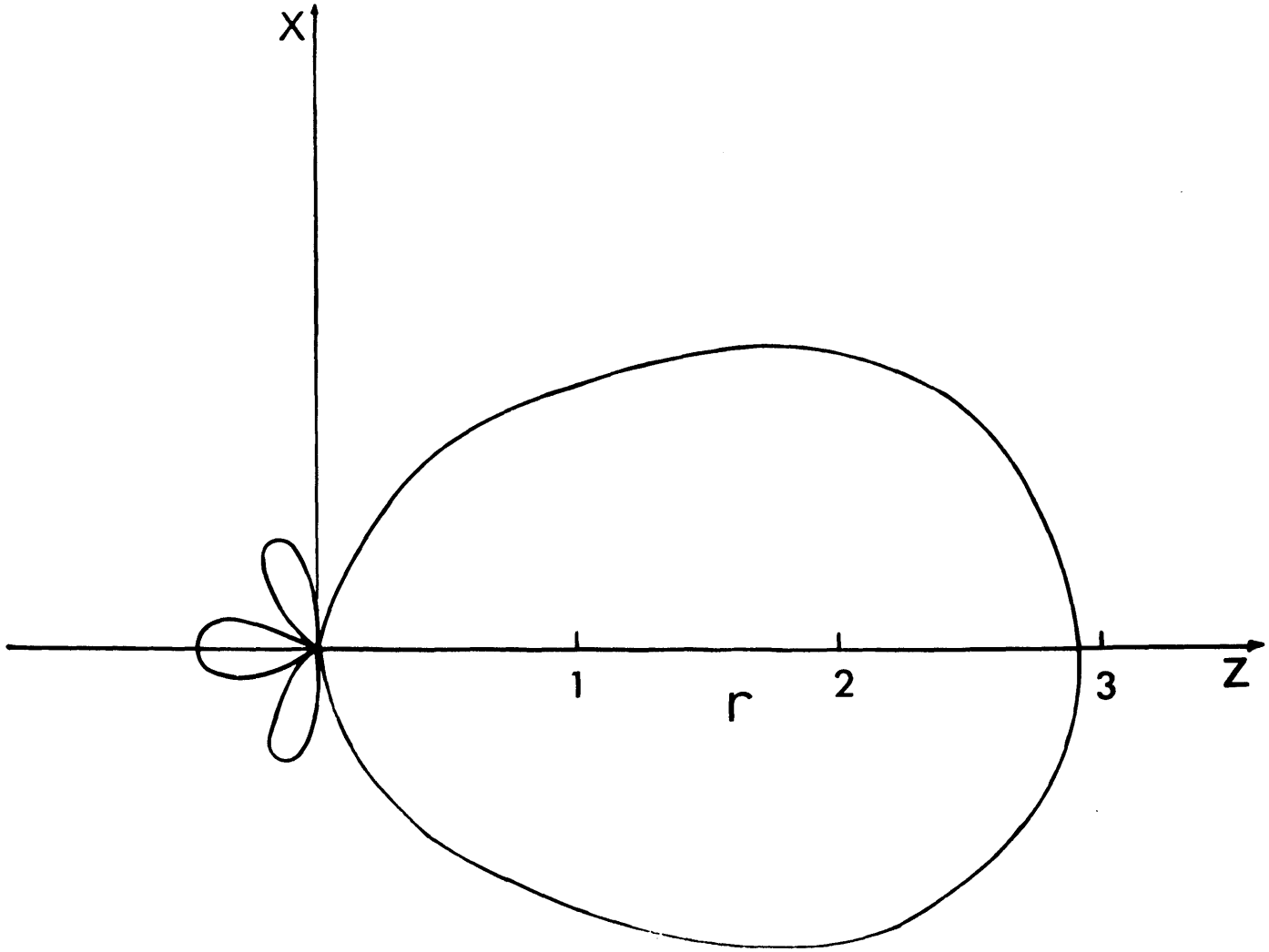


Fig. 2. The angular dependance of an octahedral hybrid orbital suitable for bond formation in the z direction.

bond may be obtained from the values of the angular portions of the wave function in the direction of their maximum extension. The orbital functions are firstly scaled such that for the s orbital the angular function is unity, Accordingly the octahedral hybrid above has a strength of 2.924, this being the valueof

$$\frac{1}{\sqrt{6}}\left(1 + \sqrt{3}\,.\sqrt{3}\,.\cos\theta + \sqrt{2}.\frac{\sqrt{5}}{2}\left(3\cos^2\theta - 1\right)\right)$$

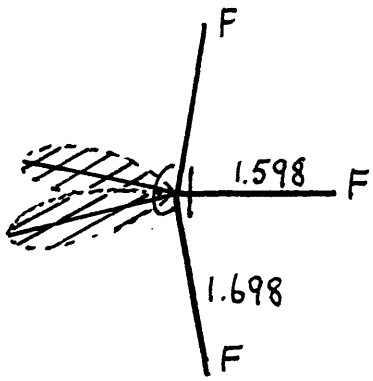
when $\theta = 0$. A pertinent application of this criterion is to that group of molecules whose structure is thought to be based upon a set of trigonal bipyramidal orbitals. These include ClF_3, SF_4 and PCl_5. If the central atom is restricted to an sp^3d^1 configuration an axial hybrid and an equatorial hybrid orbital are defined by

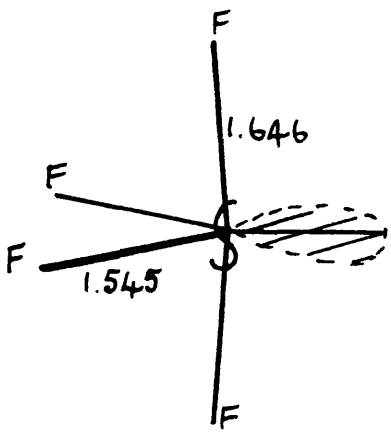
$$\psi_{axial} = \frac{1}{\sqrt{2}} \cdot \left(\cos\alpha.s + p_z + \sin\alpha\,.d_{z^2}\right)$$

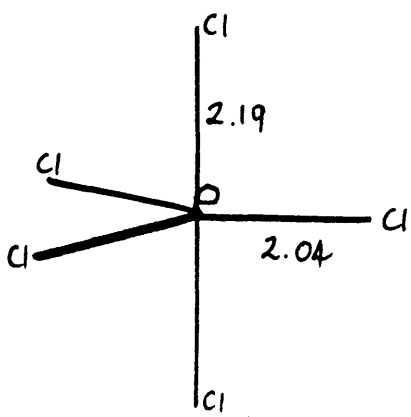
$$\psi_{equatorial} = \frac{1}{\sqrt{3}} \cdot \left(\sin\alpha.s + \frac{1}{\sqrt{2}}\,p_x - \cos\alpha\,.d_{z^2}\right)$$

where α is a hybridisation parameter. The total bond strength is a maximum when $\cos\alpha = 0.5424$. However for this value of $\cos\alpha$, the strength of the equatorial hybrid is 2.249 and of the axial hybrid 2.937. The experimental evidence indicates the opposite, namely that the equatorial bonds are stronger than the axial bonds. The structures of ClF_3 [17], SF_4 [18] and

PCl_5 [19] clearly show that the bonds are inequivalent, with the axial bonds weaker than the equatorial bonds. This view is further supported by the force constants obtained from the vibrational spectrum of PCl_5, k(axial) being 1.80×10^5 dynes/cm and k(equatorial) 2.89×10^5 dynes/cm [20].







If the central atom is not restricted to an sp^3d^1 configuration but allowed to vary as $sp^{1+2n}\ d^{3-2n}$, where $0 \leq n \leq 1$, the most favourable configuration is found to be for $n = 4/9$. For this configuration, $sp^{1\frac{8}{9}}\ d^{2\frac{1}{9}}$, the equatorial orbitals exceed the axial in strength, the respective values being 2.963 and 2.928 [21].

The Application of Maccoll's Criterion

An attempt to assess the influence of the radial wave function on the bond strength was first made by Craig, Maccoll, Nyholm, Orgel and Sutton in their definitive paper of 1954 on 'Chemical Bonds involving d-orbitals' [22]. Maccoll's criterion, introduced four years earlier, was employed [23]. This suggests that a better guide to the relative strengths of bonds might be provided by the overlap integral, for the orbitals involved in the bond. On finding for phosphorus pentachloride and sulphur hexafluoride that the contribution to the total overlap from the 3d orbitals is insignificant itis concluded for these molecules 'it is not obvious that d hybridisation can occur' A further result reached, is pertinent to the previous discussion of the relative strengths

of the axial and equatorial bonds in phosphorus pentachloride. The overlap criterion indicates that for an sp^3d^1 configuration of phosphorus, the equatorial bonds should be stronger than the axial bonds, as is observed. A view which has been reiterated more recently [24].

In evaluating the required overlap integrals Slater functions are used to represent the radial wave functions. Slater functions are nodeless functions of the form

$$R(r) = N. r^{n-1} . e^{-kr}$$

where the orbital exponent $k = Z_{eff}/n$ and N is a normalisation factor. The effective nuclear charge Z_{eff} is determined from Slater's Rules [25]. One may observe that the maximum in the probability distribution function $D(r) = r^2 R^2(r)$ will lie at a value of $r(max) = n^2/Z_{eff}$ atomic units. (1 atomic unit = 0.529 Å). In Figure 3 R(r), P(r) and D(r) are shown for a Slater 3d orbital with $Z_{eff} = 1.83$.

On applying Slater's Rules to the sp^3d^2 configuration of sulphur the effective nuclear charges for the valence electrons are found to be Z_{eff} (3s) = Z_{eff} (3p) = 6.15 and Z_{eff} (3d) = 1.65.

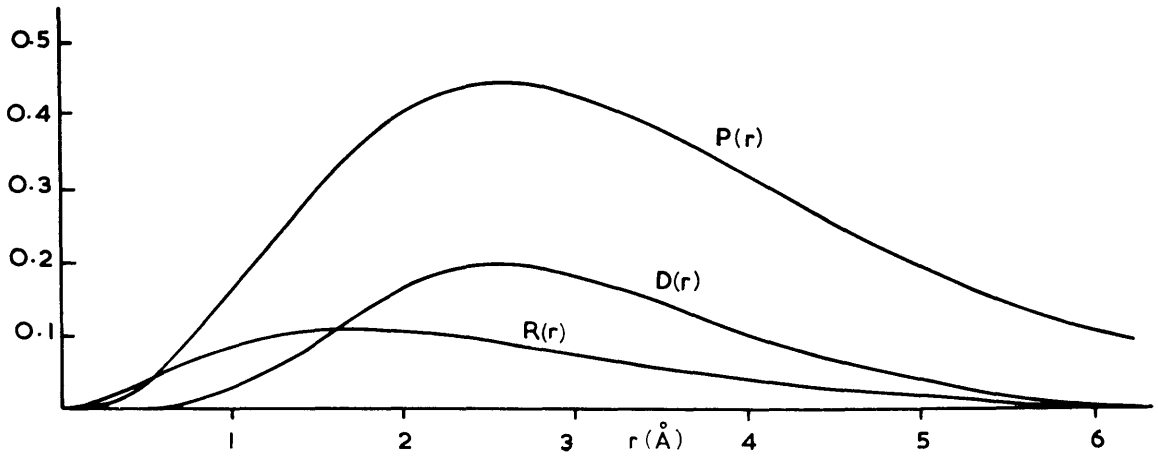


Fig. 3. Radial functions R(r), D(r) and P(r) for a hydrogenic 3d orbital with $Z_{eff} = 1.83$.

For these values the maximum in D(r) lies at 0.77 Å for the 3s and 3p electrons, and 2.88 Å for the 3d electron. The d orbital is so seen to be highly diffuse with the maximum in D(r) lying well beyond the S - F distance in SF_6 of 1.50 Å [26]. It is scarcely surprising that on this basis the d orbital contribution to the binding is found to be insignificant. Here lies a crucial point. Is the basis sound? Are Slater's rules applicable in this instance? Do Slater functions provide an adequate representation for a 3d radial function? The authors under discussion judge that 'it seems probable that the disparity in exponents while somewhat exaggerated, is essentially correct, at least for the free atoms.

When the present study was commenced in 1963 the questions raised by this paper still awaited an answer. This is not to say that in the intervening period the subject stagnated. Indeed it flourished as never before. Numerous ideas were presented to explain the structures of molecules whose central atoms are second row elements. It is just that in the absence of any knowledge of the properties of outer d orbitals, a spirit of optimism prevailed.

In the interest of cogency not all of this work is mentioned here but reference to it may be sought in a recent article entitled 'Orbitals in Sulphur and its Compounds'[96]. A principle aim now was to find a mechanism by which the diffuse 3d orbitals might effectively engage in molecular binding. Two hypothesies evolved,which might be named,the contraction theory and the charge conjecture.

The Contraction Theory

This theory, developed by Craig and his collaborators, contends that in a molecule the field imposed by the ligands upon the central atom produces an increase in the effective nuclear charge of an outer 3d orbital,thereby causing it to contract. In their original model [27] the ligands are simulated by point charges whose potential is represented by the leading term of the series expansion for 1/r. Under this spherical potential the effective nuclear charge for a 3d orbital of sulphur in SF_6 is found on minimising the total energy to increase from the Slater value for the free atom of 1.65 to 3.00. The valence orbitals so become of a comparable size. This

theory has subsequently been refined [28] and later in this study will be closely examined. The following observation might however be made at this point.

That the orbitals possessed by a free atom may bear but a slight resemblance to the orbitals of that atom when a constituent of a molecule may be recognised in the early studies upon the hydrogen molecule and its positive ion. In their calculation on H_2^+, Finkelstein and Horowitz treated the nuclear charge as a variable parameter to be determined by minimising the molecular energy. At the equilibrium bond length, the nuclear charge was found to be 1.228, corresponding to a contraction of the 1s orbital in the molecule as compared with the free atom. Since there is only one electron present this effect is entirely due to the second nucleus.

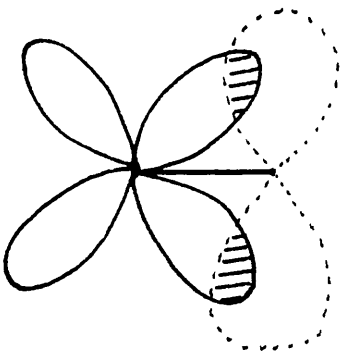
Following Rosen's example Dickinson introduced a degree of 2p character into the wave function for the positive ion.

$$\Phi = \psi_{1s_A}(z) + \psi_{1s_B}(z) + \sigma\left\{\psi_{2p_A}(z') + \psi_{2p_B}(z')\right\}$$

At the equilibrium internuclear distance of 1.06 Å, the energy is minimised for Z(1s) = 1.247, Z(2p) = 2.868 and σ = 0.145. The corresponding molecular energy differs from the observed value for H_2^+ by only 0.05 e.v. as compared with 0.53 e.v. when the 2p terms are omitted. In the ion the 2p function has contracted to such an extent that the maximum in the distribution function occurs at 0.74 Å, which is within the H - H distance. For the free hydrogen atom the 2p orbital is diffuse, with a maximum lying at 2.12 Å. The inclusion of the 2p orbital which is well separated in energy from the 1s orbital, is seen to be very important, yet to describe the bond as an sp hybrid would seem quite improper. This is a point to which I shall return.

The Charge Conjecture

The discussion so far has pertained to the use of outer d - orbitals in σ binding. As Craig et alia [22] illustrate, d-orbitals may also engage in π bonding. Here the diffuse character of the d-orbital permits the orbital to overlie a pπ orbital upon an adjacent atom as depicted.

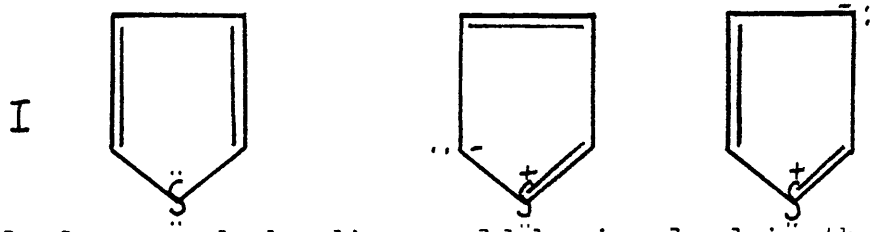


Indeed the overlap may be quite substantial. For a C - S bond, with the orbital exponent of C($2p\pi$) twice that of S($3d\pi$), the overlap is of the order of 0.4. Although this is large, since the charge is not concentrated in the region between the nuclei, it would be misleading to equate this high degree of overlap with the formation of an exceptionally strong bond. $d\pi$ - $p\pi$ bonding might so be expected to occur in thiophene, as was originally suggested by Schomaker [29] and later substantiated by the molecular orbital calculations of Longuet-Higgins[30] and most recently Bielefeld and Fitts [31].

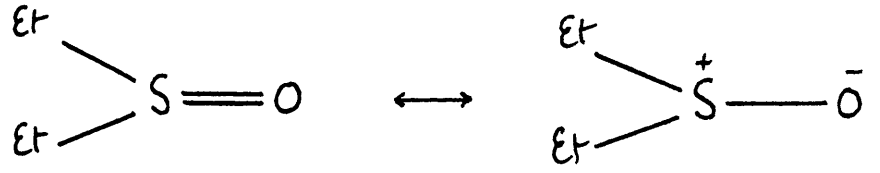
It was pointed out by Jaffe [32], Bergson[33] and others that for the neutral atom, Slater's rules indicate that the effective nuclear charge of the d orbital which might be involved in π bonding is zero. They assert that for the formation of $p\pi$ - $d\pi$ bonding it is necessary for the second

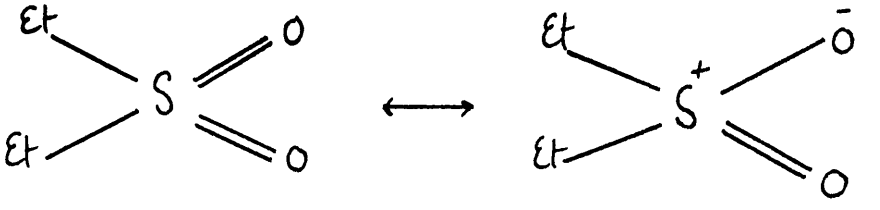
row atom to carry a positive charge, in order that $Z_{eff}(3d)$ may increase, and that atoms without such a charge cannot be expected to form $p\pi - d\pi$ bonds. This is called here, the charge conjecture. Jaffe proceeds to estimate $Z_{eff}(3d)$ in various molecules by evaluating the positive charge on the central atom with the aid of Pauling's relation for the ionic character of a bond.

The sulphur atom in thiophene may bear a positive charge if bond structures other than I are admitted.

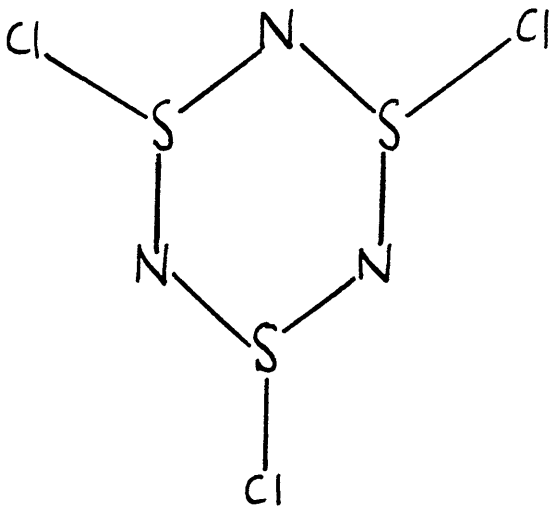


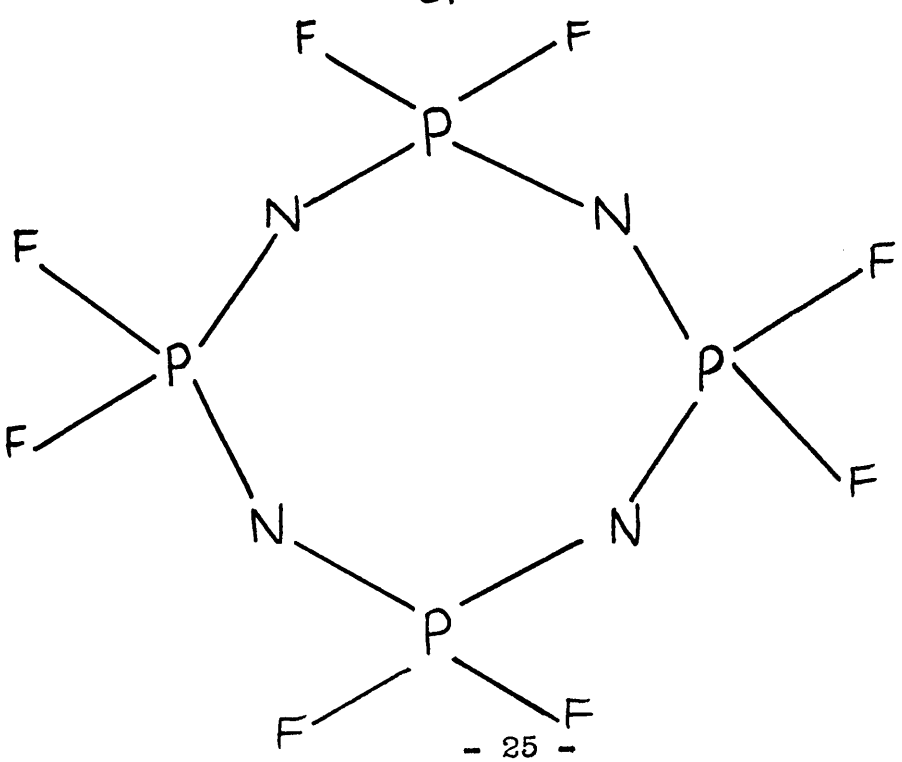
Similarly $p\pi - d\pi$ bonding could be involved in the S - O bond of sulphoxides and sulphones.





Moffit's pioneer calculations tend to support such a suggestion [34]. The manner in which the $d_{x^2-y^2}$ and d_{z^2} orbitals of the second row elements might engage in π bonding with $p\pi$ oxygen orbitals, in their oxanions is illustrated in Figure 4 [35]. It also seems likely that $p\pi - d\pi$ bonding might be present in the phosphonitrilic and thiazyl halides[36].





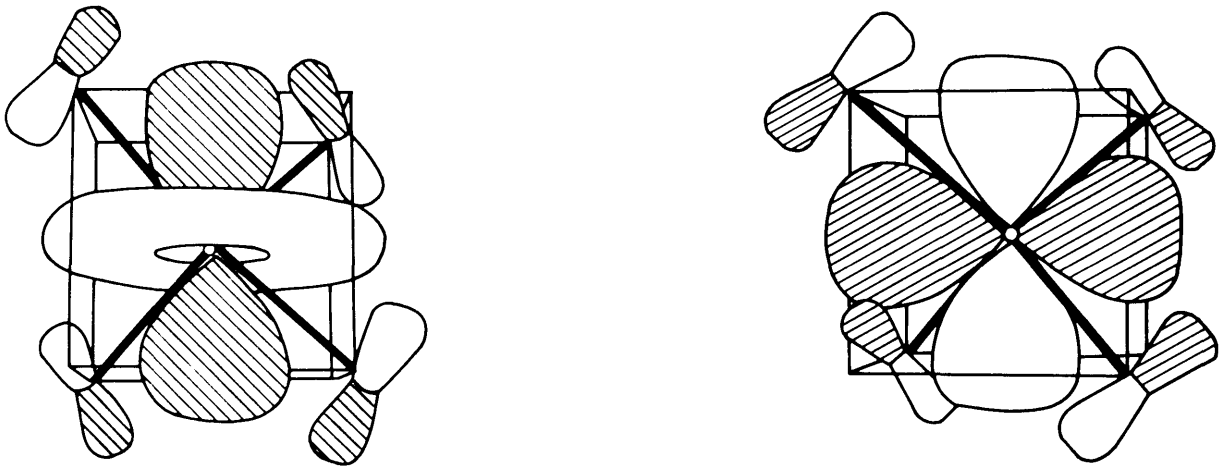


Fig. 4. An illustration of the overlap possible between $d_{x^2-y^2}$ or d_{z^2} and $2p\pi$ orbitals of oxygen in tetrahedral oxyanions.

Estimation of the Effective Nuclear Charge $Z_{eff}(3d)$.

To the present, the values employed for $Z_{eff}(3d)$, in for example overlap integrals, have been obtained by hopeful conjecture. There are no self consistent field wave functions available for the second row atoms in excited configurations. Several years ago McDougal calculated some Hartree functions for Si^{4+} [37] and Donley for Si^{3+} and Si^{2+} [38]. Boys quotes eight functions for various configurations of S and Cl but they only involve 3s and 3p orbitals [39]. More recently Watson has presented a set of accurate analytic Hartree-Fock functions for the ground states of Si, P, S, and Cl [40]

As well as Jaffe, others have contended that in their original form Slater's rules are inadequate for treating outer d electrons, in that they underestimate the extent to which the d orbital penetrates inner orbitals. This is, one may recall, contrary to the conclusion reached by Craig et alia.

Following Angus [41], Syrkin and Belov [42] modified Slater's rules with respect to the d electron, by ascribing a screening number of 0.85 instead of unity to orbitals of the same principal quantum number as the d orbital. On this basis

$Z_{eff}(3d)$ for the d orbital of $S(sp^3d^2)$ is 2.25. Cruickshank attempted to obtain an estimate of $Z_{eff}(3d)$ from self consistent field calculations on the transition metal ions [35]. Here again it appeared that by Slater's rules $Z_{eff}(3d)$ is highly underestimated. Mulliken had made similar observations [43].

Of late, Slater's rules have been superceeded by others based on analytical Hartree Fock calculations for the ground states of atoms [44]. Burns' rules indicate $Z_{eff}(3d)$ for $S(sp^3d^2)$ to be 3.4 . Clearly the size to be attributed to the 3d orbital of S in $S(sp^3d^2)$ is an open choice within a possible range of 1.40 Å to 2.89 Å for r_{max}. To describe this situation as unsatisfactory is an understatement.

The Energy of the d Orbital

Although considerable study has been made of the relative sizes of the valence orbitals for second row elements, little has ever been said about their energies. Indeed the third requirement for hybrid formation usually has been glossed over. The principal reason for this neglect is that very little information concerning the energy of

d orbitals may be gleaned from experimental sources. This is unfortunate but not irremediable.

Arndt and Eistert,better known for their organic syntheses,propagated the view that since argon is chemically inert,the energy required to promote an electron to a 3d orbital is probably prohibitive,and in consequence sulphur is unlikely to expand its valence shell [45]. Employing Moore's valuable compilation of spectroscopic data [46], Jaffe ascertained the orbital energies for some second row elements [47]. These are collated in Table I.

Table I

Orbital Energies of Second Row Elements.(e.v.)

	2p	3s	3p	3d	4s
Si	98	13.6	8.15	2.54	3.23
P	128	17.5	11.0	2.25	4.04
S	162	20.2	10.4	1.94	3.83
Cl	201	24.6	13.0	-	4.09

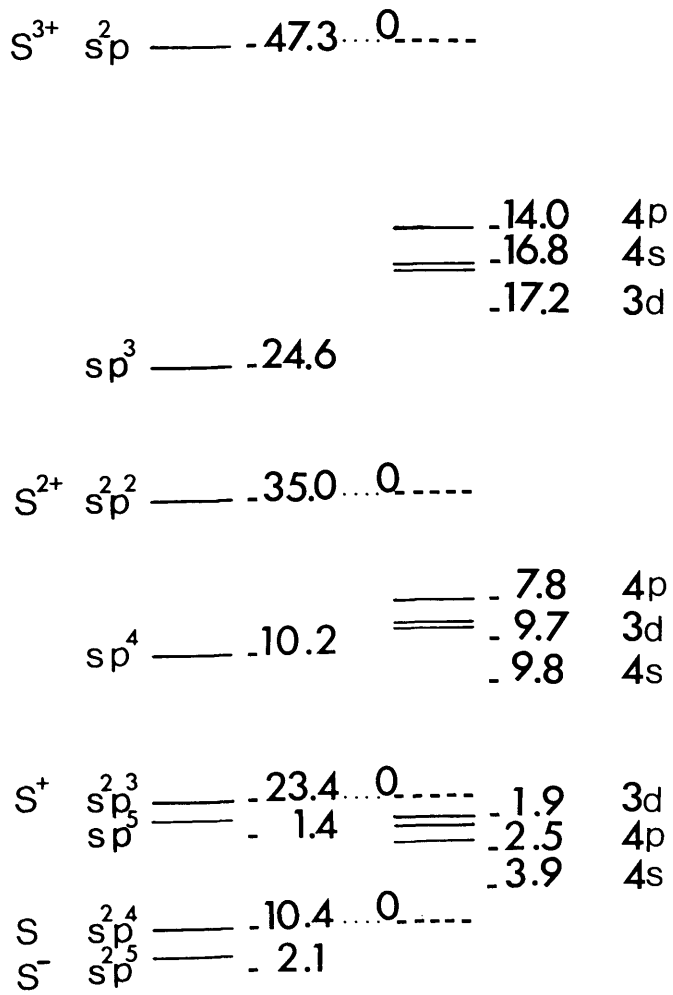
The energy required to promote a 3s electron in sulphur to the 3d level is seen to be quite substantial,amounting to 18.26 e.v. In considering these values one should remember they refer to d^1 configurations,as in $S(s^2p^4 \rightarrow S(s^2p^3d^1)$,and it is

assumed the excitation process is adiabatic, implying that no account is taken of any reorganisation which may occur on promotion. In this sense they are really pseudo - orbital energies. Some atomic energy levels for sulphur and its ions are shown in Figure 5. The levels on the left refer to the lowest term for each configuration, the ionisation potential being quoted in each case. For example the energy required to ionise the p electron of $S(s^2p^4) \rightarrow S^+(s^2p^3)$ is 10.4 e.v. whilst the electron affinity of $S(s^2p^4) \rightarrow S^-(s^2p^5)$ is 2.1 e.v. On the right of the figure are pseudo-orbital energies for the 3d, 4p and 4s orbitals of sulphur. All numbers are relative to the next zero above. It may be seen that although for neutral sulphur the energy of a d orbital is very small, - 1.9 e.v.,as sulphur acquires a positive charge, it increases quite markedly,being -9.7e.v. in S^+ and -17.2 in S^{2+}.

Conclusion

When viewed against the backcloth of a century's speculation current ideas on bonding stand out as being highly sophisticated. Superficially, the theory appears to be satisfactory

Fig. 5. Ionisation potentials and pseudo orbital energies for sulphur and its ions(e.v.). Each number is relative to the next zero level above. Thus $S^{+}(s^2p^3)$ is 23.4 e.v. below $S^{2+}(s^2p^2)$.



in that it provides a simple lucid language in which many chemical facts may be interpreted. Yet is also apparent that it is founded on quicksands. Clearly it would be highly desirable to establish whether d orbitals of second row elements are capable of assuming a role in molecular binding. This need is all the more pressing in view of recent opinions that they are totally unsuitable for such a task. A view based on no more facts than have been given here.[48]. The studies now to be presented are an attempt to clarify this situation. If they had been made long ago,as indeed they should,much ambiguity would have been dispelled,and time saved. That they have been so long in appearing is due to the fact that they are perhaps more arduous than erudite.

The core of this thesis is the calculation and interpretation of numerical self consistent field wave functions for the second row atoms Si, P, S, Cl,and Ar in configurations which involve d orbitals. After considering the self consistent field equations and the methods for their solution, the concept of the valence state is analysed. Results of self consistent field calculations are

presented and these lead one to a study of the energies of d orbitals. The theory of d orbital contraction is examined. Finally the role of d orbitals in the bonding of second row elements is reassessed. However let us now turn our attention to the self consistent field equations.

CHAPTER II

THE THEORY OF THE SELF CONSISTENT FIELD

> I have no hesitation in saying that,from a philosophical point of view,I do not believe in the actual existence of atoms,taking the word in its literal signification of indivisible particles of matter. I rather expect that we shall someday find,for what we now call atoms,a mathematico-mechanical explanation which will render an account of atomic weights,of atomicity and of numerous other properties of so called atoms.
>
> F. A. Kekule 1867.

Introduction

An exact solution of the wave equation for a system of n electrons,excepting hydrogen,is as yet unattainable. One of the most successful approaches to an approximate solution has been provided by the self consistent field method. The germs of this theory may be discerned in pre wave mechanical discussions of atomic structure but in its present form it originates from Hartree's

paper of 1928 [49].

Hartree approximates the n electron wave function $\psi(r)$ by a single product of n one electron functions $\phi(nl;r)$ each electron being assumed to move in a central field, of potential $V(r)$, produced by the nucleus and the spherically averaged charge distribution of the other electrons.

$$\psi(r) = \phi(nl;r_1) \ldots\ldots\ldots \phi(nl;r_n)$$

where

$$\phi(nl;r) = \frac{P(nl;r)}{r} \cdot S_{lm}(\theta, \phi)$$

As earlier $S_{lm}(\theta, \phi)$ is a spherical harmonic of degree l and order m. $P(nl;r)$, the radial wave function is a solution of the equation

$$\left[\frac{d^2}{dr^2} + 2V(r) - \varepsilon_{nl} - \frac{l(l+1)}{r^2}\right] P(nl;r) = 0$$

One may note that $P(nl;r) = r.R(nl;r)$. From some initial value for $V(r)$ this equation is solved for all $P(nl;r)$ subject to the boundary conditions $P(nl;0) = 0$, $P(nl;r) \to 0$ as $r \to \infty$. With these functions a new potential is evaluated and the process repeated until on successive iterations the field and wave functions remain unaltered. The field is then said to be self consistent. Hartree's procedure was critically examined by Gaunt[50], and Slater[51] demonstrated that the

self consistent field equations may be derived by applying the variation method.

The most serious deficiency of the single product wave function is that it does not satisfy the Exclusion Principle or the Principle of Identity of Electrons. Consider the 1s 2p configuration of helium, assuming an approximate wave function ψ has been obtained by Hartree's method.

$$\psi(x) = \phi(1s;r)\ \phi(2p;r)\ u_{\alpha 1} \cdot u_{\beta 2}$$

The co-ordinate $x = (r,u)$ consists of a space co-ordinate r, and a spin co-ordinate u. This really represents a set of twenty four degenerate functions since there are three 2p orbitals, corresponding to $m = +1, 0, -1$ and each electron may possess a spin of $\pm \frac{1}{2}$. Further by interchanging the co-ordinates of each electron this number of functions is doubled, producing 24 functions in all. The Pauli Exclusion principle requires that the total wave function should be antisymmetric with respect to the interchange of any pair of electrons. Consequently half of the 24 functions may be discarded since they are symmetric under such an operation.

A wave function which fulfils the requirements of the Exclusion Principle and the Principle of

Identity of Electrons may be obtained from the Hartree product by employing the antisymmetrisation operator A.

$$A = (n!)^{-\frac{1}{2}} \sum_{P} (-1)^{p} . P$$

where p is the parity of the permutation and the sum extends over all permutations.

$$\Phi(x) = A . \phi_1(nl;r_1)u_{\alpha 1} \ldots . \phi_n(nl;r_n)u_{\beta n}$$

$$\Phi(x) = (n!)^{-\frac{1}{2}} \sum_{P} (-1)^{p} . P \; . \phi_1(nl;r_1)u_{\alpha 1} \ldots . \phi_n(nl;r_n)u_{\beta n}$$

$$\Phi(x) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(nl;r_1)u_{\alpha 1} & \phi_2(nl;r_1)u_{\beta 1} \ldots \phi_n(nl;r_1)u_{\beta n} \\ \phi_1(nl;r_2)u_{\alpha 2} & \phi_2(nl;r_2)u_{\beta 2} \ldots \\ \vdots & \vdots \\ \phi_1(nl;r_n)u_{\alpha n} & \ldots\ldots\ldots\ldots \phi_n(nl;r_n)u_{\beta n} \end{vmatrix}$$

This wave function, first introduced by Dirac [52] was subsequently widely employed by Slater [53] whose name it nowss bears. Using this determinantal wave function as a starting point, Fock[54] and independantly Dirac [55] derived the self consistent field equations including exchange, or more briefly the Hartree-Fock equations. Lennard-Jones soon presented a more elegant analysis by way of the density matrix[56]. Here but a brief outline of the original formulation is given, to introduce the notation of the self consistent field equations.

This follows Hartree in 'The Calculation of Atomic Structures'[57].

The Self Consistent Field Equations

The Hartree-Fock equations are obtained by applying the variation principle to the total energy of an atom, whose total wave function is approximated by a Slater determinant or a linear combination of such determinants. On integrating over the angular variables, the total energy $E = \int \Phi^{\dagger} H \Phi \, d\tau$ may be expressed in terms of radial integrals as

$$E = \sum_{n\ell} q(n\ell) I(n\ell) + \sum \frac{1}{2} q(n\ell)[q(n\ell) - 1] F_0(n\ell, n\ell)$$
$$+ \sum_{n\ell, n'\ell' \neq n\ell} q(n\ell) q(n'\ell') F_0(n\ell, n'\ell')$$
$$- \sum_{n\ell k} A_{\ell k} F_k(n\ell, n\ell) - \sum_{n\ell, n'\ell', k} B_{\ell\ell' k} G_k(n\ell, n'\ell')$$

The radial integrals occurring in this expression are defined by

$$I(n\ell) = -\frac{1}{2} \int_0^\infty P(n\ell; r) \left[\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2} \right] P(n\ell; r) dr$$

$$F_k(n\ell, n'\ell') = \int_0^\infty \int_0^\infty P^2(n\ell; r) P^2(n'\ell'; s) U_k(r, s) dr ds$$

$$G_k(n\ell, n'\ell') = \int_0^\infty \int_0^\infty P(n\ell; r) P(n'\ell'; r) U_k(r, s) \cdot P(n\ell; s) P(n'\ell'; s) dr ds$$

$$U_k(r, s) = r^k / s^{k+1} \quad \text{if } r \leq s$$
$$= s^k / r^{k+1} \quad \text{if } r > s$$

The coefficients A_{lk} and $B_{ll'k}$ may be evaluated from tables of Slater coefficients, $a_k(lm_l,l'm_{l'})$ and $b_k(lm_l,l'm_{l'},$. Their values depend upon which configuration and multiplet of an atom is being considered. One may note that for a configuration involving two or more incomplete groups nl, n'l' the expression for E carries an additional term $-\sum_{k>0} C_{ll'k}F_k(nl,n'l')$. By demanding that the energy E shall be a minimum for small variations in the radial functions P(nl;r), subject to the orthonormality constraints

$$\int_0^\infty P^2(nl;r) = 1$$

$$\int_0^\infty P(nl;r)\,P(n'l';r) = 0 \quad nl \neq n'l'$$

the Hartree-Fock equations are obtained. They are of the form

$$\left[\frac{d^2}{dr^2} + \frac{2Y(nl;r)}{r} - \varepsilon_{nl,nl} - \frac{l(l+1)}{r^2}\right]P(nl;r) = X'(nl;r)$$

where $Y(nl;r) = Z - \sum_{n\ell} q(nl)Y_0(nl,nl;r)$

$$+Y_0(nl,nl;r) + \frac{2}{q(nl)}\sum_{k\neq 0} A_{lk}Y_k(nl,nl;r)$$

$$+ \frac{1}{q(nl)}\sum_{k\neq 0} C_{ll'k}Y_k(nl,nl;r)$$

$$X'(nl;r) = X(nl;r) + \sum_{n\neq n'} \varepsilon_{nl}\varepsilon_{n'l}\,P(n'l;r)$$

$$X(nl;r) = -\frac{2}{q(nl)}r\sum_{n'l'\neq nl} B_{ll'k}Y_k(nl,n'l';r)P(n'l';r)$$

and $Y_k(nl,n'l';r) = r\int_0^\infty U_k(r,s)P(nl;s)P(n'l';s)ds$

If the exchange terms are eliminated by placing $X'(nl;r) = 0$ the equations reduce to those for the Hartree wave function but here the charge distribution has not been spherically averaged. On omitting terms with $k > 0$ one naturally obtains the conventional form for Hartree's equations.

$$\left[\frac{d^2}{dr^2} + \frac{2Y(nl;r)}{r} - \varepsilon_{nl,nl} - \frac{l(l+1)}{r^2} \right] P(nl;r) = 0$$

Due to the presence of the exchange terms the solution of the Hartree-Fock equations is somewhat arduous, as compared with the relative ease with which the Hartree equations may be solved. In order to retain this simplicity of solution and yet preserve the essential characteristics of the Hartree-Fock functions, Slater proposed that the exchange potentials, which clearly differ for each wave function, might be replaced by a single potential which is the same for all the wave functions and formed by suitably averaging the individual exchange potentials [58]. If it is further assumed that the average exchange potential depends only on the charge density in the region of a particular electron, the average exchange potential may be identified with that obtained by Bloch for a free electron gas. This potential

has the form

$$V_{exchange}(\rho) = 6\left[\frac{3}{8\pi} \cdot \rho\right]^{\frac{1}{3}}$$

where $\rho(r)$ the spherically averaged total charge density is given by

$$\rho(r) = \frac{1}{4\pi r^2} \cdot \sum_{n\ell} P(nl;r)^2$$

When $V_{exchange}(\rho)$ is incorporated in the self-consistent field equations in place of the proper exchange terms, the equations are known as the Hartree-Fock-Slater equations, and are of the form

$$\left[\frac{d}{dr^2} + \frac{2Y(nl;r)}{r} + V_{exchange} - \varepsilon_{nl,nl} - \frac{l(l+1)}{r^2}\right] P(nl;r) = 0$$

At small and at large distances from the nucleus these equations are not entirely satisfactory. Latter[59] attempted to ensure that the correct asymptotic behaviour is observed at large values of r, where the total potential should naturally tend to $-Z/r$, by switching to this potential

$$V(r) = -Z/r$$

at that value of r when $\frac{2Y(nl;r)}{r} + V_{exchange} = -\frac{Z}{r}$.

Of the self consistent field equations, the Hartree-Fock equations provide the best approximate solutions of the wave equation for an atomic system. They are approximate in that the interaction between pairs of electrons, $\frac{e^2}{r_{ij}}$ cannot be exactly

represented by a sum of one particle interactions.

Were r_{ij} to equal zero the electron interaction would become infinite. Consequently electrons prefer to keep apart from each other. The Hartree-Fock method allows for this in that electrons of the same spin to the one being considered, are caused to move away from the neighbourhood of this particular electron, through the operation of the exclusion principle. It is as if one unit of charge is removed from the system, at the position of the electron under consideration, leaving a positive hole. This is indeed referred to as the Fermi hole. The principle feature of the Hartree-Fock-Slater method is to replace the Fermi holes of each electron, which are different, by a spherical hole of radius proportional to $\rho^{-1/3}$, for every electron.

Since the electrons of like spin remain at further distances from the electron considered in the Hartree-Fock method, as compared with the Hartree method, which takes no account of the Fermi hole, the coulomb repulsion $\frac{e^2}{r_{ij}}$ is less in the Hartree-Fock approach, than in the Hartree. The potential energy is therefore correspondingly lower in the former method. This effect will be reflected in

the shape of the wave functions, and the orbital energies, obtained by the two methods. The Hartree-Fock wave functions should be more compact than the Hartree functions with lower orbital energies, whilst Hatree-Fock-Slater functions should occupy an intermediate position. As will be shown the difference between Hartree and Hartree-Fock wave functions for the 3d orbitals of the second row elements is far greater than might ever have been anticipated.

The Solution of the Self Consistent Field Equations.

At the present time there are two general methods for solving the self consistent field equations. One of these, which will not concern us here, consists in expanding the unknown wave function ϕ_i in terms of a set of linearly independent basis functions $\chi_i \ldots \chi_m$

$$\phi_i = \sum_{j=1}^{m} c_{ij}\chi_j$$

and determining the coefficients c_{ij} by solving the appropriate secular equation. The accuracy with which the resulting set of analytical wave functions match the true Hartree-Fock solutions clearly depends on the choice of the basis set, but even with a minimal basis set it is high. Watson[60]

Clementi [61] and others utilising the original techniques of Roothaan [62],have generated tables of analytic Hartree-Fock functions for most of the elements and their ions in ground state configurations.

The second method consists in solving the self consistent field equations directly by a numerical approach. Hartree in his first paper [49] presented a detailled outline of the numerical procedure required to obtain a solution of the self consistent field equations,without exchange, and later extended this to equations with exchange. The method is admirably delineated in his book,to which reference has been made earlier. Applications of the numerical solution of the self consistent field equations,prior to 1950 have also been surveyed by Hartree [63],whilst a bibliography up to 1958 is annotated by Slater[64]. It is interesting to note that it was not until September 1958 that a truely self consistent solution of the Hartree-Fock equations for an open 3d shell was reported. This was by Worsley[65] for $V^{2+}(3s^2 3p^6 3d^3)$.

The numerical solution of the self consistent field equations may be divided into three stages:

(1) The evaluation and tabulation of the potential functions $Y(nl;r)$ and $X(nl;r)$.

(2) The integration of each equation, subject to the appropriate boundary conditions.

(3) The repetition of these two processes until self consistency is attained to the required accuracy.

(1) Evaluation of $Y(nl;r)$ and $X(nl;r)$.

The calculation commences by estimating a set of initial wave functions. These are often taken to be of a hydrogenic type with suitably selected screening numbers. To obtain $Y(nl;r)$ and $X(nl;r)$ it is necessary to evaluate the functions from which they are compounded, namely $Y_k(nl,n'l';r)$. As Hartree shows (section 3.5) this may be defined as a solution of a pair of equations which involve an auxillary function $Z_k(nl,n'l';r)$. These are

$$\frac{dZ}{dr} = P(nl;r)\, P(n'l';r) - \frac{k}{r} Z$$

and $$\frac{dY}{dr} = -\frac{(2k+1)}{r} Z + \frac{k+1}{r} Y$$

with the boundary conditions $Z(0) = 0$ and

$Y_k(r) - Z_k(r) \to 0$ as $r \to \infty$

On changing the variable to $t = \log_e r$ the equations assume the form

$$\frac{dy}{dx} = ay + f(x) \qquad \text{----------(a)}$$

where a is a constant and f(x) is a known function

$$\frac{dZ}{dt} = -kZ + rP(nl;r)\,P(n'l';r)$$

$$\frac{dY}{dt} = (k+l)Y - (2k+l)Z$$

If $a < 0$ this equation is stable for integrating outwards from $x = 0$ and consequently the first equation may be solved for Z by integrating outwards to the boundary from a small value of r. A starting value may be obtained from the relation Z(r)

$$Z(r) = \frac{r.P(nl;r)\,P(n'l';r)}{(l+l'+k+3)} \quad \text{for small r}$$

These values for Z may then be used to solve the second equation which is stable to integration inwards from the boundary condition $Z(r) = Y(r)$. The solution of equation (a) is given by

$$\frac{d}{dx}\left(e^{-ax}y\right) = e^{-ax} f(x)$$

whence using a central difference formula to evaluate the integral $\int_{x}^{x+h} e^{-ax} f(x)\,dx$ one obtains the result

$$y(x+h) = Ay(x) + Bf(x-h) + Cf(x) + Df(x+h) + Ef(x+2h) \ldots\ldots$$

where $A = e^{ah}$, $B = \frac{-h}{24}.e^{2ah}$, $C = \frac{13h}{24}\,e^{ah}$,

$D = 13h/24$, and $E = \frac{-h}{24}\,e^{-ah}$.

Substituting a = k the outward integration is readily accomplished, whilst with a = k+1 and the corresponding relation for y(x-h) the inward integration is performed. Two features should be noted. Firstly, this method of integration differs from that suggested by Hartree, in that a change in variable is made. This leads to a very swift and accurate integration procedure for obtaining Y(nl;r) and X(nl;r). For a configuration comprising of several groups this is a major part of the total calculation. Secondly, for the self consistent field equations without exchange there are no terms with k > 0 and the problem reduces to solving Poisson's equation $\frac{d^2Y(nl,n'l';r)}{dr^2} = \frac{P(nl;r)P(n'l';r)}{r}$ which presents no difficulty.

(2) The integration of the equations.

The problem is to obtain a solution of the equation

$$\left[\frac{d^2}{dr^2} + \frac{2Y(nl;r)}{r} - \varepsilon_{nl} - \frac{l(l+1)}{r^2}\right] P(nl;r) = X'(nl;r)$$

where Y(nl;r) and X(nl;r) are known and ε_{nl} is a parameter to be determined such that the wave functions satisfy the boundary conditions $P(0)=P(\infty)=0$ and normality requirement $\int P^2(nl;r)dr = 1$.

Orthogonality

It may be recalled that X'(nl;r) contains terms involving the off diagonal parameters $\varepsilon_{nl,n'l'}$ which appear through the constraint that the wave functions be orthogonal. For a configuration of complete groups it may be shown that the wave functions are necessarily orthogonal and in consequence a satisfactory solution is obtained by placing $\varepsilon_{nl,n'l} = 0$. When the groups are incomplete, $\varepsilon_{nl,nl}$ may be adjusted in the following way. Consider P(nl;r) and P(n'l;r) to have been obtained as solutions to the equations

$$\left[\frac{d^2}{dr^2} + \frac{2Y(nl;r)}{r} - \varepsilon_{nl} - \frac{l(l+1)}{r^2}\right]P(nl;r) = X(nl;r) + \frac{1}{q_{nl}}\varepsilon_{nl,n'l}P(n'l)$$

$$\left[\frac{d^2}{dr^2} + \frac{2Y(n'l;r)}{r} - \varepsilon_{n'l} - \frac{l(l+1)}{r^2}\right]P(n'l;r) = X(n'l;r) + \frac{1}{q_{n'l}}\varepsilon_{nl,n'l}P(nl)$$

With some slight manipulation one may obtain ε_{ij} as

$$\varepsilon_{ij} = \left(\frac{q_{nl}\cdot q_{n'l}}{q_{nl}-q_{n'l}}\right)\int_0^\infty \left[\frac{2[Y(nl;r)-Y(n'l;r)]}{r}P(nl)P(n'l) + P(nl)X(n'l) - P(n'l)X(nl)\right] dr$$

Any required alteration in ε_{ij} as the calculation proceeds may so be estimated. When there are a number of open groups of the same l, the procedure becomes rather complex and to the present no satisfactory manner of adjusting all the off diagonal

parameters involved, has been devised. Also for configurations where $q_{nl} = q_{n'l}$ this method is clearly invalid. An example of such an anomaly is provided by helium in the excited state 1s'2s'. ^{1}S[66].

The integration process

For small values of r the term in $\frac{l}{r}2$ dominates in the radial equation, which becomes

$$\frac{d^2P(r)}{dr^2} - \frac{l(l+1)}{r^2} P(r) = 0$$

This equation has two solutions $P(r) = r^{l+1}$ and r^{-l}. Since $P(0) = 0$ only the former solution is acceptable. At large values of r, P(r) behaves as $\exp(-r\sqrt{\varepsilon_{nl}})$. Betweem these two limits P(r) is sinusoidal in character. This suggests that for stability in integration one should integrate outwards from small r, inwards from the boundary and match the two solutions at an intermediate point.

The choice of the method for performing the integration is important. Four of the more common difference methods have been investigated by Froese [67]. She found that of Numerov to be the most efficient and this has been employed here. Numerov's method is based on the relation between the second derivative f'' of a function and its second difference

$$\delta^2 f_j = h^2[\, f_j'' + \tfrac{1}{12}\delta^2 f_j'' \,]$$

where h is the interval length. In a version of a self consistent program of my own, I used the integration procedure exemplified by Hartree. [section 4.4]. This was quite satisfactory, but requires one to guess a second difference as the integration proceeds. Although quite realisable, a computer takes considerable more time 'to guess' than does a human agent, and the extensive use of this method is not recommended.

The outward integrations are initiated by utilising a series expansion for P(r)

$$P(r) = Ar^{l+1}[1 - \left(\frac{Z}{l+1}\right)r + Br^2 + Cr^3]$$

where $B = [\, 2Z^2 - l(l+1)(2V_o - \varepsilon_{nl})] \,/\, 2(2l+3)(l+1)$

and $C = Z[2Z^2 - (3l+4)(2V_o - \varepsilon\ )] \,/\, 6(l+1)(l+2)(2l+3)$

V_o is the potential at the nucleus due to all the electrons of the atom, other than the one under consideration, as is indicated by the prime.

$$V_o = \int_o^\infty \frac{\sum' q(nl)\, P^2(nl;r)}{r}$$

The parameter $A = \underset{r \to 0}{Lt}\left(\frac{P(r)}{r^{l+1}}\right)$ is directly related to the initial slope of the wave function and is a means by which the normality condition is maintained during the course of a calculation. Often its value is required quite accurately and

for this purpose the radial equation is transformed into two first order equations for integration at small r. On making the substitution

$$s(r) = \frac{P(nl;r)}{r^{l+1}}$$

$$q(r) = [\frac{dP}{dr} - \frac{l(l+1)}{r}. P(nl;r)]. \frac{1}{r^{l+1}}$$

the radial equation may be written as

$$\frac{ds}{dt} = rq$$

$$\frac{dq}{dt} = [r\varepsilon_{nl} - 2Y(nl;r)]s - 2(l+1)q + r.\frac{X(nl;r)}{r^{l+1}}$$

where as previously $t=\log_e(r)$. A is now accessible as s(o). This pair of equations are integrated outwards until

$$\frac{l(l+1)}{r} < 2Y$$

when P(r) is no longer of the form r^{l+1}.

The integration continues with the complete equation

$$\frac{d^2F(nl;r)}{dt^2} + [2r.Y(nl;r) - \varepsilon_{nl}.r^2 - (l+\tfrac{1}{2})^2]F(nl;r) = r^{3/2}. X(nl;r)$$

in which the substitution $F(t) = P(r).r^{-1/2}$ has been made to eliminate the first derivative dP/dt. On reaching a point r(j) where

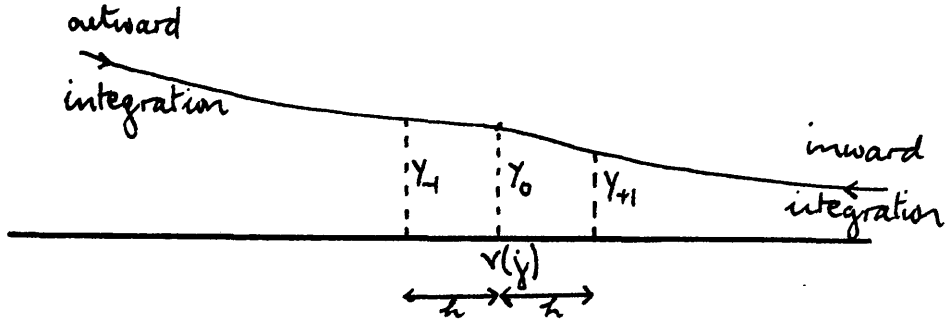
$$2rY(nl;r) - \varepsilon_{nl}.r^2 - (l+\tfrac{1}{2})^2 < 0$$

the integration is carried on for just two more intervals r(j1),r(j2).The inward integration is now commenced from an estimated value of λ for $P(r_b)$

at the boundary, and performed until r(j) is reached. When P(r,j1) and P(r,j2) are the same for the outward and inward integrations the matching is complete.

A match of the outward and inward integrations together with the maintenance of normality is accomplished by adjusting the parameters ε_{nl}, A, and λ. At this stage the solution is far simpler for the equations without exchange for since they are homogeneous A and λ become scaling factors and only ε_{nl} needs to be corrected.

In the early stages of the outward integration ε_{nl} is adjusted by a simple doubling or halfing process so that the required number of nodes for the wave function have been passed and the function is decreasing, by the time r(j) is reached. There are a number of iterative schemes for adjusting the then current values of ε_{nl} to ensure a smooth join is obtained. Froese discusses the relative merits of those due to Ridley [68] and Cooley[69]. I found the latter method to be very efficient. This simply corrects the eigenvalue ε_{nl} by the amount that Numerov's equation remains unsatisfied at the join r(j).



$$\varepsilon' = \varepsilon + \mathrm{Res}$$

$$\mathrm{Res} = \delta^2 y_o - h^2\left[y_o'' + \frac{\delta^2 y_o''}{12} \right]$$

Mayers has a different scheme by which ε, A, and λ may be simultaneously corrected[70]. This too is very effective; provided A has been estimated with reasonable accuracy it can force convergence from estimates of ε_{nl} and λ which are in error by a factor of 100 or more.

It may be noted that if all the estimates for the three parameters are very bad, there is at the present no satisfactory systematic procedure for their correction.

(3) The self consistent solutions.

Having obtained a solution of the radial equation for a particular electron one now needs to consider the most direct route to self consistency. This is primarily a matter where experience comes to the

fore,particularly when dealing with 3d orbitals which are highly sensitive and usually require several iterations to reach self consistency. Two points deserve to be mentioned.

It is usually more effective to attain self consistency of the outermost group,before considering the inner groups at all. The inner groups are then taken singly,moving back to the outermost at the end of each cycle. For example in treating $S(sp^3d^2)$ 3d is iterated to self consistency, then 3p, followed by 3d,until P(3d) and P(3p) are self consistent. The 3s orbital is then taken followed by the core orbitals,which usually converge quite swiftly. At the beginning of the process,time is conserved if only a low self consistency criterion is imposed. For example one might dictate that self consistency is attained when the results differ by 0.1 . When all the groups are self consistent to this accuracy,their refinement to a higher degree of self consistency is extremely fast.

On commencing the calculation from an initial estimated wave function,it is not generally satisfactory,for outer orbitals,to employ the corresponding solution as the input for the next iteration. A simple device for improving estimates

is to compound the new estimate $P^2(nl;r)$ from the original one $P^1(nl;r)$ amd the corresponding solution $P^{sol}(nl;r)$ by way of the relation

$$P^2(nl;r) = (1-\gamma)\, P^{sol}(nl;r) + \gamma P^1(nl;r)$$

When $\gamma = 0$ the new input is provided by the preceeding solutions, which is satisfactory for core orbitals. For outer orbitals γ may assume values up to as high as 0.5 .

A method which I have found to work very well for outer orbitals involves the input and output of two successive iterations, In(1), In(2), Out(1), and Out(2). The input for the next iteration In(3) is taken as

$$In(3) = Out(1) + \beta[Out(2) - Out(1)]$$

where $$\beta = \frac{Out(1) - In(1)}{[Out(1) - In(1)] - [Out(2) - In(2)]}$$

Computer Programmes

Four main programmes have been used to obtain the self consistent field functions which are presented in this study. The Hartree-Fock wave functions were calculated with the user code programme written by D.F.Mayers for the Mercury computer at Oxford. This has since been superceeded, and is no longer available. Hartree-Fock-Slater wave functions have been obtained by adapting the IBM 7090 Program of Hermann and Skilmann[71] to

meet the requirements of the Atlas Computer at S.R.C. Harwell. The modifications required to ensure the reliable running of this Fortran programme were trivial,but extended over a considerable time period due to the unknown and changing features of the machine.

Hartree functions without exchange have been generated from two programmes written in ALGOL for the English Electric KDF 9. One of these was written by myself,the other which appeared later was devised by D.F.Mayers. I chose to continue with the latter for it incorporated a more accurate integration procedure than my own and was,generally,not so coarsely hewn. It has however as yet no ancillary features and provides but a set of self consistent functions on a logarithmic grid together with the parameters ε_{nl} and A. This output is therefore employed as data to another programme which by interpolation produces a set of functions on an evenly spaced grid,and calculates such material as the energy of the configuration,the mean radii of the functions,the effective nuclear charges at the origin,and performs an analysis of the orbital energies.

It might be added that except where convergence

set of wave functions for a configuration of a
difficulties are met, the calculation of a second row element including d orbitals, using the Kidsgrove compiler, without optimiser, requires of the order $\simeq 8$ minutes computing time. On Atlas $\simeq 3$ minutes is the norm.

Multiplet Structure

In the opening paragraphs it was seen that the simple product of one electron functions employed by Hartree really represents a set of degenerate wave functions. Such a set of functions and their energy level is known as a configuration. In general a configuration is $2^n(2l+1) \ldots (2l_n+1)$ degenerate but of this set only a few functions, $\prod_i^{} 2(2l+1)C_{q_{nl}}$ conform to the exclusion principle. For example of the 14,500 functions for sp^3d^2 only 1,800 satisfy the exclusion principle.

As was also remarked earlier, the linch pin of the self consistent method is the replacement of the interaction between two electrons by a sum of one particle interactions. The resulting Hamiltonian so becomes invariant under the seperate rotation of the co-ordinates of each electron and the one electron functions are of a central field type, transforming as the representation D^{ℓ} of the rotation group.

However the true Hamiltonian is only invariant under a simultaneous transformation of the electron co-ordinates, though since spin orbit coupling is excluded, the space and spin co-ordinates may be treated seperately. The wave function Φ will so transform as

$$D^{l_1} \times D^{l_2} \times D^{l_3} \ldots = \Sigma D^{L}$$

under a rotation of all of the space co-ordinates and as

$$D^{\frac{1}{2}} \times D^{\frac{1}{2}} \ldots = \Sigma D^{S}$$

under a rotation of the spin co-ordinates. Further, it may be seen that the degeneracy of the configuration is lowered, by the emergence of a series of multiplets, or terms, each of which is $(2S+1)(2L+1)$ degenerate.

Let us consider the terms which arise from an sp^3d^2 configuration. This is achieved in the customary manner by determining the terms for s, p^3, and d^2 configurations separately and then coupling them together to obtain those terms which evolve from the sp^3d^2 configuration. Russell-Saunders coupling is assumed to be applicable. For example the configuration p^3 represents 216 states of equal energy from which twenty one terms could arise. Through the operation of the exclusion principle

this is reduced to twenty states and three terms. The permissible terms may be found in the manner originally described by Slater[53].

The various possible assignments of the quantum numbers m_l and m_s for the three p electrons which are in accord with Pauli's principle are listed in Table 2. The notation $(1^+, 1^-, 0^+)$ implies that electron 1 has $m_l = +1$, $m_s = +\frac{1}{2}$; electron 2, $m_l = +1$, $m_s = -\frac{1}{2}$; and for electron 3, $m_l = 0$, $m_s = +\frac{1}{2}$.

Table 2

M_s / M_L	$+\frac{3}{2}$	$+\frac{1}{2}$
2		$(1^+,1^-,0^+)$
1		$(1^+,0^+,0^-),(1^-,-1^+,1^+)$
0	$(1^+,0^+,-1^+)$	$(1^+,0^+,-1^-),(1^+,0^-,-1^+)$ $(1^-,0^+,-1^+)$

This is but a segment of the complete table which is naturally repeated for $M_S = -\frac{1}{2}, -\frac{3}{2}$ and $M_L = -1, -2$.

Commencing with the state $(1^+, 1^-, 0^+)$, this clearly originates from a ^2D term. Such a term is ten fold degemerate and the other nine states associated with this term may be selected from the

central section of the table from M_L = +1 to -2 and $M_s = +\frac{1}{2}$ and $-\frac{1}{2}$. There remains one state with M_L = +1 and $M_S = +\frac{1}{2}$ indicating the presence of the six fold degenerate term ^2P. Four states are left unaccounted, and these are seen to belong to a quartet, ^4S. Due to electron interaction, the configuration p^3, accordingly splits into three terms ^4S, ^2D, ^2P.

Similarly it may be shown that the configuration d^2 generates five terms, ^3D, ^3P, ^1G, ^1D, and ^1S. When these two sets are coupled and the result coupled with the doublet ^2S term of the s^1 configuration 110 terms are obtained, represinting in all the 1,800 states mentioned previously, for the configuration sp^3d^2. They are:

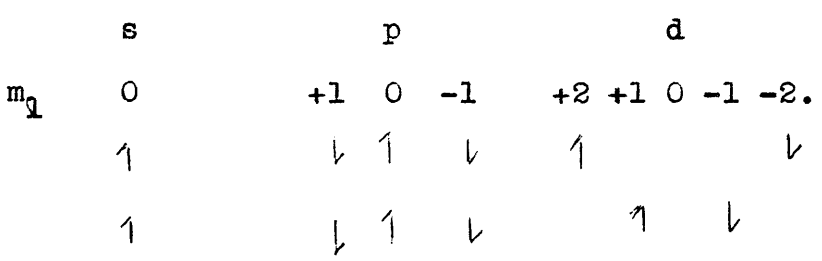
2^1S, 7^1P, 8^1D, 8^1F, 5^1G, 3^1H, ^1I.

4^3S, 11^3P, 13^3D, 12^3F, 8^3G, 4^3H, ^3I.

2^5S, 5^5P, 5^5D, 5^5F, 3^5G, ^5H.

^7P, ^7F.

Several terms are seen to occur more than once. For example there are two ^1S terms. The difference between them may be represented schematically in a familar way.



In such circumstances the derivation of the self consistent field equations is complicated. Aterm chosen for study should preferably be unique.

When faced with this host of terms for $S(sp^3d^2)$ it is natural to ask which are pertinent to a study of the shape and energy of the d orbital. In an attempt to find a basis for making a suitable choice let us now consider the concept of the valence state.

CHAPTER III

THE CONCEPT OF THE VALENCE STATE

It is rumoured that the group pest is gradually being cut out of quantum physics.

H. Weyl 1928.

Introduction

The purpose of this chapter is twofold. Firstly, I wish to show what meaning is to be attached to statements of the form 'in SF_6 the sulphur atom is sp^3d^2 hybridised' and secondly to find which of the 110 terms of this configuration participate in the valence state of sulphur in SF_6. The 'valence atate' is a term which has been woven into many chemical discussions, so simply, that when the fabric of the argument is viewed from a distance, its presence is hardly discernible. On closer scrutiny it emerges as a barbed and elusive concept. Many semi-empirical molecular orbital calculations refer their parameters to the valence state, yet the concept of the valence state has been defined only in valence bond theory. Indeed its very definition seems to have

presented difficulty.

The Valence State of Carbon in Methane, CH_4.

Referring to the carbon atom in methane, Van Vleck states that 'the spins of the four electrons belonging to sp^3 are assumed paired with those of the four atoms attached by the carbon . Such a condition of the carbon atom we may conveniently call its valence state It is not identical with any one of the six atomic states of carbon and is instead to be regarded as a linear combination of these'[72]. In the same year 1934,Mulliken writes 'the term'valence state' introduced by Van Vleck,describes a certain hypothetical state of interaction of the electrons of an atomic electron configuration'. Apparently unsatisfied with this as a definition he continues 'a 'valence state' is an atom state chosen so as to have as nearly as possible the same condition of interaction of the atom's electrons with one another,as when the atom is part of a molecule.' Yet again in the next sentence 'a valence state of an atom is one in which the latter's valence electrons behave towards one another as if each

were paired somehow with a valence electron of a foreign atom,but not with any valence electron of the given atom'[73]. With these definitions only a particular coupling scheme is admitted for the molecule,that appropriate to perfect electron pairing. For the carbon atom in methane this is only one of fourteen possible couplings,and for the sulphur atom in SF_6 one out of 132. The advantage of such a restriction lies in that the energy of the atom in the valence state is directly accessible from the energy expression appropriate to perfect pairing. For the carbon atom in methane the energy of the valence state referred to the ground state $(s^2p^2,\ ^3P)$ is so obtained as

$$E_{vs} = I(3s) + 3I(3p) + \sum_{ij} Q_{ij} - \frac{1}{2}\sum_{ij} J_{ij}$$

where the spins of the four electrons are taken as being entirely independent of each other. It is sometimes said that since in the valence state the spins are random,there is an equal chance of the spin of two electrons being parallel or oppossed,and hence their exchange integral enters the expression weighted by a factor of $\frac{1}{2}$. More accurately,when the spins are oppossed the exchange interaction is + J,associated with a singlet state,and when parallel -J referring to

a triplet state. Since there are four possible spin couplings of which three correspond to a triplet state and one to a singlet the exchange interaction is $+\frac{1}{4}(+J) + \frac{3}{4}(-J) = -\frac{1}{2} J$.

Later definitions of the valence state are more general in character. Pauling writes quite succinctly 'the valence state of an atom is defined as that state in which it has the same electronic structure as it has in the molecule'[74]. Coulson 'the valence state is a hypothetical state where the valence orbitals are in a condition suitable for maximum overlap but in which the spins are random'[75]. Kotani 'the valence state of an atom in a molecule is the state of this atom which is obtained when all the other atoms in the molecule are removed to infinite distances, subject to the condition that the wave function of the total electronic system is kept rigidly fixed [76]. Finally, Moffitt 'valence states of atoms are defined so that the intra-atomic couplings of the spins of their electrons correspond closely to those which may occur when the atom becomes part of a molecule' [77].

All of these authors are attempting in a

variety of ways to describe the condition of the atom in the molecule. It is not at all clear to me that there should be such an entity, but even accepting the postulate, the valence state seems to have eluded definition. Consider the original statements of Van Vleck and Mulliken. They appear to be quite specific and a formula is provided from which the valence state energy may be adduced. For a carbon atom forming four hybrids the valence state energy is given by the expression

$$E_{vs} = \tfrac{1}{4}(1-\mu)[F_o(2s,2s)-2F_o(2s,2p)+F_o(2p,2p)]$$
$$-\tfrac{1}{2}(19+2\mu)F_2(2p,2p)+\tfrac{1}{2}(-5+2\mu)G_1(2s,2p)$$

where μ is a hybridisation parameter. When $\mu = \frac{1}{4}$ the energy refers to a basis of four tetrahedral hybrids, $h_1^1\ h_2^1\ h_3^1\ h_4^1$, each of which is singly occuppied. When $\mu = 1$ the energy pertains to the sp^3 configuration of carbon. Clearly in any discussion of valence state it is essential to define ones basis.

Let us examine more closely the case of four singly occupied equivalent hybrids $h_1^1\ h_2^1\ h_3^1\ h_4^1$ commonly described as V_4.

$$E(h_1^1\ h_2^1\ h_3^1\ h_4^1) = I(2s)+3I(2p)+3/16\ F_o(2s,2s)$$
$$+\tfrac{21}{8}F_o(2s,2p)+\tfrac{51}{16}F_o(2p,2p)$$
$$-\tfrac{39}{4}F_2(2p,2p)-\tfrac{9}{4}G_1(2s,2p)$$

Table 3

Term Energies for Configurations of Carbon

s^2p^2	^3P	$2I(2s)+2I(2p)+F_o(2s,2s)+F_o(2p,2p)+4F_o(2s,2p)$ $-5F_2(2p,2p) - 2G_1(2s,2p)$
	^1D	$2I(2s)+2I(2p)+F_o(2s,2s)+F_o(2p,2p)+4F_o(2s,2p)$ $+F_2(2p,2p) - 2G_1(2s,2p)$
	^1S	$2I(2s)+2I(2p)+F_o(2s,2s)+F_o(2p,2p)+4F_o(2s,2p)$ $+10F_2(2p,2p) -2G_1(2s,2p)$
sp^3	^5S	$I(2s)+3I(2p)+3F_o(2p,2p)+3F_o(2s,2p)$ $-15F_2(2p,2p) - 3G_1(2s,2p)$
	^3D	$I(2s)+3I(2p)+3F_o(2p,2p)+3F_o(2s,2p)$ $-6F_2(2p,2p)-2G_1(2s,2p)$
	^3P	$I(2s)+3I(2p)+3F_o(2p,2p)+3F_o(2s,2p)-2G_1(2s,2p)$
	^3S	$I(2s)+3I(2p)+3F_o(2p,2p)+3F_o(2s,2p)$ $-15F_2(2p,2p) + G_1(2s,2p)$
	^1D	$I(2s)+3I(2p)+3F_o(2p,2p)+3F_o(2s,2p)-6F_2(2p,2p)$
	^1P	$I(2s)+3I(2p)+3F_o(2p,2p)+3F_o(2s,2p)$
p^4	^3P	$4I(2p)+6F_o(2p,2p) - 15F_2(2p,2p)$
	^1D	$4I(2p)+6F_o(2p,2p) - 9F_2(2p,2p)$
	^1S	$4I(2p) + 6F_o(2p,2p)$

From this expression for the energy it is evident that the hybrid valence state will involve configurations of carbon other than sp^3, since no term in the latter may possess a contribution from $F_o(2s,2s)$. The term energies of the s^2p^2, sp^3 and p^4 configurations of carbon, expressed in Slater Condon parameters, are contained in Table 3. There one can see that $F_o(2s,2s)$ arises from but the s^2p^2 configuration, as is only to be expected. To obtain $\frac{3}{16} F_o(2s,2s)$ and equivalence of the I(nl) integrals so requires the valence state energy to be compounded as

$$E_{vs} = \frac{3}{16} E(s^2p^2) + \frac{5}{8} E(sp^3) + \frac{3}{16} E(p^4)$$

Further, utilising the theory of the symmetric permutation group it may be shown that only specific terms of each configuration will be involved in the valence state. They are ^3P, ^1D of s^2p^2 and p^4 together with ^5S, ^3D and ^1D of sp^3. Also, as Serber [81] shows, the number of states of multiplicity $(2S + 1)$ arising from n orbitals is $^nC_k - {}^nC_{k-1}$ where $k = \frac{n}{2} - S$. The total number of states is 2^n. Hence in the valence state where the

spin is random, and all spin possibilities must be considered, the total weight with respect to spin of each multiplet is $\frac{(2S+1)({}^{n}C_{k} - {}^{n}C_{k-1})}{2^{n}}$

In the present example n=4, whence the total weight of quintets is $\frac{5}{16}$, triplets $\frac{9}{16}$ and singlets $\frac{1}{8}$. There is only one quintet, $sp^3\ {}^5S$. This therefore will appear in a decomposition of E_{vs} as a sum of spectroscopic terms with the coefficient $\frac{5}{16}$. Noting that of the two terms of s^2p^2 or p^4, the triplet will have three times the spin wieght of the singlet, the weightings of all of the other terms follows immediately. It is given by the expression

$$E_{vs} = \frac{9}{64}(s^2p^2,\ {}^3P) + \frac{3}{64}(s^2p^2,\ {}^1D) + \frac{5}{16}(sp^3,\ {}^5S) + \frac{9}{32}(sp^3,\ {}^3D) + \frac{1}{32}(sp^3,\ {}^1D) + \frac{9}{64}(p^4,\ {}^3P) + \frac{3}{64}(p^4,\ {}^1D)$$

This is just the result obtained in a different fashion by Voge[78]. However it is not as Voge declares the valence state of Van Vleck or the equivalent of the 1:1 element of his secular determinant referred to the valence state. To reproduce the expression for the valence state

energy,of Van Vleck quoted earlier,which is naturally identical with the 1:1 element,requires the spectroscopic terms to be weighted as

$$E_{vs} = \frac{9}{64}(s^2p^2,\ ^3P) + \frac{3}{64}(s^2p^2,\ ^1D) + \frac{5}{16}(sp^3,\ ^5S) + \frac{15}{32}(sp^3,\ ^3D) - \frac{5}{32}(sp^3,\ ^1D) + \frac{9}{64}(p^4,\ ^3P) + \frac{3}{64}(p^4,\ ^1D)$$

In this expression the total spin weightings are not in the proper proportions.This discrepancy arises from the spurious inclusion of $-\frac{3}{8}\ G_1(2s,2p)$ for the p^4 configuration in the averaging of the exchange terms,which is the keystone of the Van Vleck - Mulliken approach. The correct expression for the valence state energy is the first and one should not be mislead when working within the perfect pairing approximation of Van Vleck and Mulliken,into thinking that weighting of the terms is at all comparable.

To 1963,no study had been made of the valence state for an atom in an octahedral environment. A group theoretical analysis was therefore performed, with the sulphur atom in SF_6 as an example.This analysis,which now follows,utilises the theory of the symmetric permutationgroup. Of late,the symmetric group has become popularised in the development of Spin Free Quantum Chemistry.The fundamentals are laid down however in the works of Weyl[79]and Wigner[80]

whilst its use by Serber[81] should not be overlooked.

The Valence State of Sulphur in SF_6.

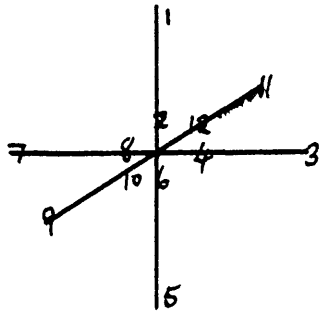
It is well known that sulphur hexafluoride is a regular octahedron. This high degree of symmetry enables one to effect a factorisation of the secular determinant for the molecule, quite readily. Since a molecule might be expected to attain its lowest energy state when the maximum number of bonds are formed, our attention might justifiably be restricted to that segment of the determinant pertaining to singlet states.

In considering the sulphur atom one has to take into account the following hybrid configurations

(1)	$h_1^1\ h_2^1\ h_3^1\ h_4^1\ h_5^1\ h_6^1$	1	132
(2)	$h_1^2\ h_2^1\ h_3^1\ h_4^1\ h_5^1\ h_6^o$	30	1260
(3)	$h_1^2\ h_2^2\ h_3^1\ h_4^1\ h_5^o\ h_6^o$	90	1260
(4)	$h_1^2\ h_2^2\ h_3^2\ h_4^o\ h_5^o\ h_6^o$	20	100

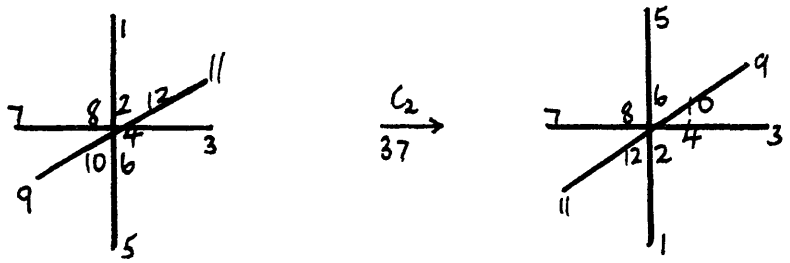
Configuration 1 is unique and will generate $^{12}C_6 - {}^{12}C_5$, or 132 singlet states. There are 30 such configurations of the type 2, each of which will give rise to 42 singlet states, and hence in toto 1260 singlet states. Similarly each of the 90 configurations of 3 will produce 14 singlets,

giving in all 1260 states,whilst the 20 configurations of type 4 will yield 100 singlets, since each gives rise to 5 singlet states. Clearly in this form the problem is intractable,as it involves a determinant of order 2752. But the state of lowest energy for a molecule is usually found to be that which is totally symmetric and one is naturally lead to consider the totally symmetric singlet states. The principles involved in applying the theory of the permutation group may be illustrated in determining how many of the 132 singlet states of configuration (1) are totally symmetric. Six equivalent hybrids,singly occupied are assumed to be provided by the central atom. These are labelled 2, 4, 6, 8, 10, and 12. The ligand orbitals,with which the hybrids overlap, are numbered 1, 3, 5, 7,9and 11. If a symmetry



operation of the group O_h is now applied these twelve integers will be permuted. For example the operation C_2 about an axis passing through orbitals 3 and7 leads to a new ordering of the integers,as is

illustrated.



This permutation may be expressed concisely in the cyclic notation as (1,5)(9,11)(2,6)(10,12)(3)(7)(4)(8).The integers in the parentheses,called a cycle,are those which have undergone an interchange on the operation of C_2. Similarly the operation C_4 about an axis passing through 1 and 5 induces the permutation (3,9,7,11)(4,10,8,12)(1)(5)(2)(6).

It is to be noted that the permution under C_2 contains four cycles composed of two elements, and four cycles of single elements. The cycles are said to be of length two and one respectively. This leads to a definition of the partition number. For a system comprising of n elements the number of possible divisions of n into positive integral summards is called the partition number of n.Thus the permutation under C_2represents a partitioning of the number 12 as

$$2 + 2 + 2 + 2 + 1 + 1 + 1 + 1 = 12$$

whilst under C_4 the partition is

$$4 + 4 + 1 + 1 + 1 + 1 = 12$$

In general the partitioning of the number n is of the form

$$\lambda_1 + \lambda_2 + \lambda_3 \ldots \lambda_p = n$$

where λ_i is the length of the cycle i and there are p cycles.

Now it is required to ascertain the characters for the representation Δ^k for the permutation of the set of twelve orbitals under the operation of the O_h group. $k = n/2 - S$ where as usual S is the total spin angular momentum. Naturally, for singlet states $S = 0$. It may be shewn that the character δ^k of the represention for a particular operation is the coefficient of x^k in the polynomial

$$(-1)^{n-p}(1-x)(1+x^{\lambda_1})(1+x^{\lambda_2}) \ldots (1+x^{\lambda_p})$$

For example the character of the representation for the permutation induced by the C_2 operation is equal to the coefficient of x^6 in the polynomial

$$(-1)^4(1-x)(1+x^2)^4(1+x)^4$$

This is +4. Continuing in this manner the total character table is constructed. It is

	E	$8C_3$	$3C_2$	$6C_2'$	$6C_4$	i	$8iC_3$	$3iC_2$	$6iC_2$	$6iC_4$
δ	132	6	4	20	4	20	2	20	4	4

This representation may be reduced in the usual

manner under the group O_h, to give

$$\Delta^6 = 10A_{1g} + 4A_{1u} + 2A_{2g} + 8E_g + 2E_u + 6T_{1g} + 6T_{1u} + 10T_{2g} + 10T_{2u}$$

Of the 132 singlet states pertaining to configuration (1) it is to be seen that only ten are totally symmetric. The magnitude of the problem is so reduced quite drastically.

A similar analysis is now performed for the configurations (2),(3) and (4). This is slightly more involved in that not all the 90 possible configurations of type (3) for example will be invariant under an operation of the group, It is therefore necessary to determine for each operation how many configurations will remain invariant and so possibly have a character different from zero. On doing this,one finds that configuration (2) gives rise to 39 singlets,configuration (3) 93 singlets and configuration (4) 8 singlets.

The problem of the valence state of sulphur in SF_6 is clearly of a different order of magnitude to that of carbon in methane. For sulphur the secular determinant for the totally symmetric singlet states of the possible hybrid configurations is 150 x 150. When all interatomic integrals are placed equal to zero,this determinant refers

directly to the valence state of sulphur in SF_6. This could well involve 150 terms of sulphur from such a variety of configurations as sp^3d^2, $s^2p^2d^2$, sp^4d^1, $s^2p^3d^1$, p^4d^2, s^2p^4, sp^5 and p^6. If only a configuration of singly occuppied hybrid orbitals is admitted then the problem reduces to one of the 10^{th} degree, and if only one coupling scheme is allowed, that appropriate to perfect pairing, to one of the first order. However as has been demonstrated earlier for carbon, the energy of the valence state within the perfect pairing approximation is compounded from the seven terms to which the 7 x 7 determinant may be referred. The question now naturally arises as to which of the 110 terms of the sp^3d^2 configuration for sulphur will appear in the determinant referring to the valence state. The theory of the permutation group allows such a selection to be made with ready ease. One has only to find which states of the sulphur atom when combined with the six ligand orbitals transform as the symmetric representation A_{1g} of the group O_h.

In the previous chapter it was observed that a multiplet consists of a set of (2L+1)(2S+1) wave functions which transform under rotation of the space co-ordinates and the spin co-ordinates

as D^L and D^S respectively. For a rotation α the characters $\chi(\alpha)$ for the representations are obtainable from the expression

$$\chi(\alpha) = \frac{\sin(L+\frac{1}{2})\alpha}{\sin \alpha/2}$$

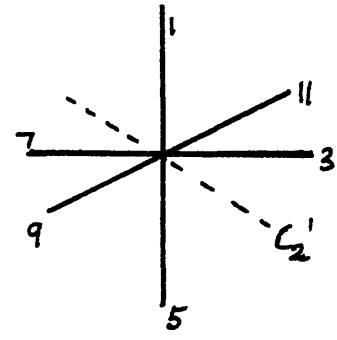
The irreducible components of the representations for a number of point groups are given by Kotani[76]. For O_h, these have been verified and are listed in Table 4 for the configuration sp^3d^2 which is ingrade.

Table 4

Term	L	States of $S(sp^3d^2)$ transform as
S	0	A_{1u}
P	1	T_{1u}
D	2	$E_u + T_{2u}$
F	3	$A_{2u} + T_{1u} + T_{2u}$
G	4	$A_{1u} + E_u + T_{1u} + T_{2u}$
H	5	$E_u + 2T_{1u} + T_{2u}$
I	6	$A_{1u} + A_{2u} + E_u + T_{1u} + 2T_{2u}$

It is now necessary to determine the manner in which the ligand orbitals will transform, when their electrons are orientated such that their total spin is 0, 1, 2, and 3. This is most readily effected

by use of the symmetric group. For example consider the operation C_2'. This induces the permutation (1,5)(3,9)(7,11) which corresponds to a partitoning of the integer six as 2 + 2 + 2. Consequently the characters for S = 0, 1, 2, and 3 are given as the coefficient of x^k, where k = 6/2 - S in the polynomial



$$(-1)^3(1-x)(1+x^2)^3$$

For S=0 the complete character table is

	E	$8C_3$	$3C_2$	$6C_2'$	$6C_4$	i	$8iC_3$	$3iC_2$	$6iC_2'$	$6iC_4$
δ	5	2	1	3	1	3	0	-1	1	-1

This representation reduces under O_h to give

$$\Delta^3 = A_{1g} + A_{1u} + T_{2g}$$

In a similar manner, the representations for the transformation of the ligand orbitals when the total spin is 1, 2, or 3 are obtained and their irreducible components determined. They are contained in Table 5.

Table 5

S	Ligand orbitals transform as
0	$A_{1g} + T_{2g} + A_{1u}$
1	$A_{2u} + E_u + T_{1u} + T_{1g}$
2	$T_{2g} + E_u$
3	A_{2u}

By comparing the ligand representations of Table 5 with those for the central atom contained in Table 4 and noting the direct products which give rise to the totally symmetric representation A_{1g}, a selection of the terms is achieved. One finds that of the 110 terms for $S(sp^3d^2)$ only the following may participate in the valence state of sulphur in an octahedral environment:

S		
0	A_{1u}	$^1S,\ ^1G,\ ^1I.$
1	A_{2u}	$^3F,\ ^3I.$
	E_u	$^3D,\ ^3G,\ ^3H,\ ^3I.$
	T_{1u}	$^3P,\ ^3F,\ ^3G,\ 2\,^3H,\ ^3I.$
2	E_u	$^5D,\ ^5G,\ ^5H.$
3	A_{2u}	$^7F.$

This is the result which Craig and Thirunamachandran

have also obtained by projection operator methods[82].

In the light of this analysis let us return now to our original intention and consider what is to be understood by the statement 'in SF_6 the sulphur atom is sp^3d^2 hybridised'. If the sulphur atom in SF_6 forms six equivalent hybrids then it is quite correct that these may be formed from a set of orbitals which contains one s orbital, three p orbitals and two d orbitals. The converse is certainly not true. Given a set of six equivalent orbitals, the condition of the sulphur atom in SF_6 may only be partially described as being in an sp^3d^2 configuration. Other configurations contribute to the state of the sulphur atom, which is evidently in a highly complex condition.

One is misled by the statement to identify the number of orbitals in the set from which the hybrids are compounded, with the occupation numbers of the orbitals. Either in SF_6 the sulphur atom is in an sp^3d^2 configuration or it is in a hybridised state as represented by the configurations (1) to (4) inclusive. Both statements cannot be true simultaneously. If the former case is taken, one is returning to an early theory of valence due to

Heitler and Rumer[83]. The latter pertains to the directed theory of valence of Slater and Pauling.

Having also ascertained which of the terms arising from the sp^3d^2 configuration of sulphur participate in the valence state, the self consistent field calculations may now be profitably pursued. Of these terms ^7F is by Hund's rules the lowest of all. This term, with ^1I, spin the manifold and are also amenable to the self consistent field method, being represented by one and two determinants respectively. They have therefore been chosen for study.

CHAPTER IV

SOME ORBITAL FEATURES

Form, which we discover in nature by analysis, is obstinately mathematical in its manifestations.

Herbert Read 1965.

Introduction

There is now to be shown the variety of shapes possessed by the valence orbitals of the second row elements mentioned earlier, together with some of their properties. Naturally much attention will be directed towards the d orbital since its features are the least known. The radial wave functions, to be illustrated, have been obtained by the numerical solution of the self consistent field equations. Where multiplets are mentioned the coefficients of the integrals in the expression for the energy of the multiplet together with the

values of the various integrals are listed in Appendix 1.

Shapes of Orbitals

Let us now look at figure 6. This contains the radial functions P(3d;r) for configurations of sulphur involving one and two d electrons respectively. The most striking feature to be observed is the considerable contraction of the 3d orbital when one passes from $S(s^2p^3d^1)\ ^5D$, curve a, or $S(sp^4d^1)\ ^5F$, curve b, to a configuration involving two 3d electrons. For the d^1 configurations the shape of the 3d orbital is almost independant of the change in occupation number of the 3s and 3p orbitals between the two configurations. One may recall that the mean radius of an orbital, designated here as

$$\bar{r}(nl;r) = \int_0^\infty P(nl;r)r.P(nl;r)dr$$

and is related to the effective nuclear charge $Z_{eff}(nl)$ by the expression

$$\bar{r} = \frac{n^2}{Z_{eff}}\left[1+\frac{1}{2}\left\{1-\frac{l(l+1)}{n^2}\right\}\right] \quad \text{a.u.}$$

For these two orbitals the mean radius is 4.01 Å and 3.85 Å respectively. The mean radius of the 3d orbital for $S(sp^3d^2)\ ^7F$, curve c is 1.89 Å . This

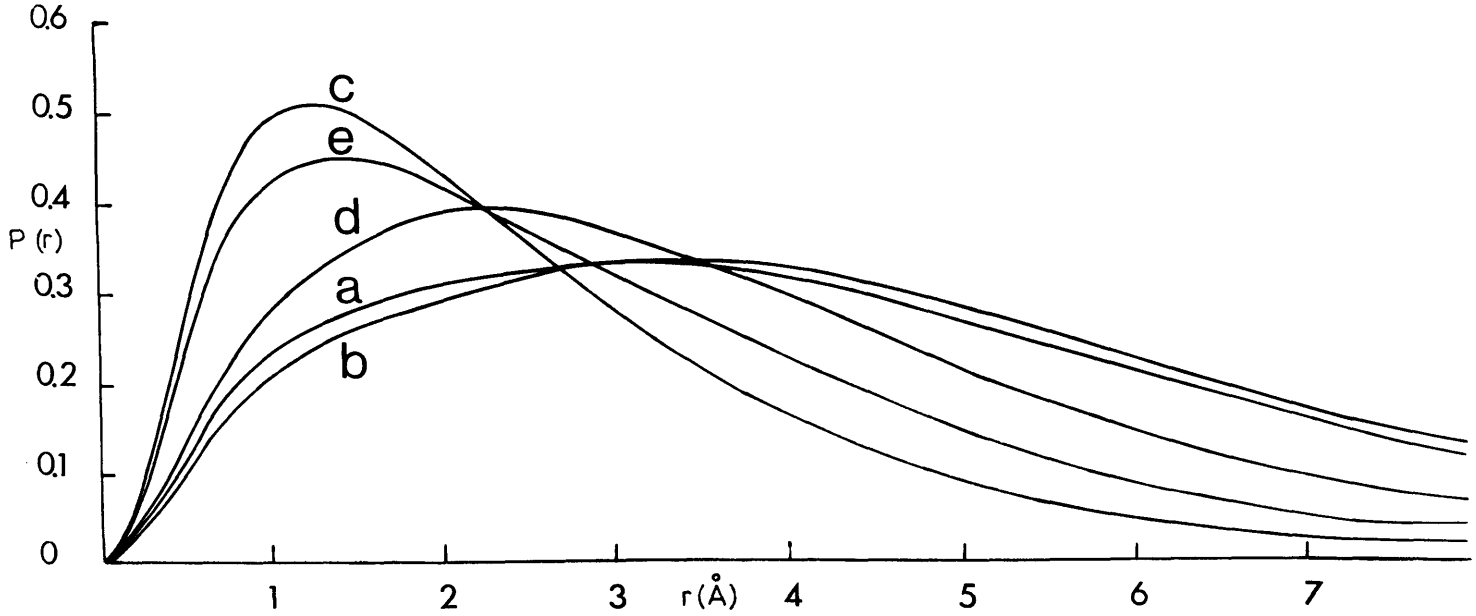


Fig. 6. Self consistent field wave functions P(r) for d^1, curves a and b, and d^2 configurations of sulphur.

corresponds to more than a twofold increase in the effective nuclear charge of the 3d orbital, which is 1.4 for the d^1 configurations and 2.95 for $(sp^3d^2)^7F$.

Amongst the d^2 configurations, there is also to be seen a large variation in orbital size. The Hartree 3d orbital for $S(sp^3d^2)$, curve d, for which of course no exchange terms are considered, has a mean radius of 3.02 Å. Between this orbital and that for the ^7F lie all the orbitals for the terms listed in the previous chapter. The intermediate curve, shown as e, does not correspond to any spectroscopic term but lies emergetically exactly midway between ^3I and ^1I, differing from both by $1/3\ G_1(3s,3p)$. It is for one of the determinants of ^1I, $(3s^{o+})(3p^{1+})(3p^{1-})(3p^{o-})(3d^{2+})(3d^{2-})$. This orbital has a mean radius of 2.30 Å.

Clearly there is a considerable latitude in the choice one might make for $Z_{eff}(3d)$ of $S(sp^3d^2)$ depending on the multiplet involved. The limits are 2.94 for ^7F and 1.85, which is the Hartree value. It is therefore important to consider as to which of the two curves correspond more closely to the 3d orbital for the valence state of sulphur, in the particular environment of interest. In an octahedral field Craig and Thirunamachandran find that for a

valence state based solely on an sp^3d^2 configuration, the 3d orbital is diffuse with a mean radius of 2.39Å. But if a valence state based on six equivalent hybrids is considered within the perfect pairing approximation, $\bar{r}$ (3d) is 1.67 Å [84]. The analytic form they have taken to represent the 3d orbital will be mentioned in a moment.

Another parameter which is of value in discussing the shapes of orbitals has been mentioned previously in Chapter II. It is

$$A = \lim_{r \to 0} \left[\frac{P(nl;r)}{r^{l+1}} \right] .$$

This is a measure of the initial slope of the wave function and may be related to the effective nuclear charge for the orbital in regions near to the nucleus. In fact it is a guide to the degree of penetration of a particular orbital. Here the effective nuclear charges appropriate to a given value of A are notated as Z^A_{eff} and evaluated from the relation

$$A = \left[Z^A_{eff} \frac{(n+l)! / (n-l-1)!}{n(2l+1)!} \right]^{\frac{1}{2}} \cdot \left(\frac{2Z^A_{eff}}{n} \right)^{l+1}$$

Thus for the Hartree 3d orbital of $S(sp^3d^2)$, A is 2.534 and $Z^A_{eff}(3d)$, 5.0 whilst for the ^7F term A = 5.9188, and Z^A_{eff} (3d) = 6.38 Naturally the higher value of A, the greater is the initial slope.

Table 6 (cont'd)

Hartree-Field (cont'd)

	3s			3p			3d		
	r_{max}	$\bar{r}$	A	r_{max}	$\bar{r}$	A	r_{max}	$\bar{r}$	A
$S^{+}(s^1p^3d^1)$	0·76	0·88	11·38	0·93	1·03	37·81	1·64	2·05	3·98
$S^{+}(s^1p^2d^2)$	0·76	0·87	11·58	0·85	0·99	39·23	1·27	1·69	5·58
$Si(s^1p^1d^2)$	0·93	1·11	8·32	1·10	1·34	22·97	2·36	3·18	1·04
$P(s^1p^2d^2)$	0·84	0·98	9·84	0·93	1·16	29·96	2·36	3·07	1·68
$Cl(s^1p^4d^2)$	0·68	0·80	12·96	0·76	0·92	46·88	2·36	3·00	3·56
$Ar(s^1p^5d^2)$	0·64	0·74	14·57	0·68	0·84	57·13	2·36	3·01	4·70
$Ar(s^1p^3d^4)$	0·63	0·72	14·94	0·68	0·80	59·90	1·02	1·70	11·56

Hartree-Fock-Slater Field

$S(s^2p^4)$	0·72		11·14	0·81		37·56	-		-
$S(s^2p^3d^1)$	0·72		11·49	0·79		40·53	2·84		4·34
$S(s^1p^4d^1)$	0·71		11·55	0·79		40·87	1·37		4·80
$S(s^1p^3d^1s^1)$	0·71		11·83	0·77		42·60	1·01		9·12
$S^{+}(s^1p^3d^1)$	0·71		11·84	0·77		42·56	1·01		9·49
$S^{+}(s^1p^2d^2)$	0·70		12·00	0·76		43·57	0·96		10·82
$S^{2+}(s^1p^2d^1)$	0·70		12·20	0·74		44·78	0·89		12·68

Table 6

The principal maxima, r_{max}, mean radii $\bar{r}$ and the parameter A for the valence orbitals of Si, P, S, Cl and Ar, obtained by numerical self consistent field methods.

Hartree-Fock Field

	3s			3p			3d		
	r_{max}	$\bar{r}$	A	r_{max}	$\bar{r}$	A	r_{max}	$\bar{r}$	A
$S(s^2p^4)\ ^3P$	0·76	0·91	9·98	0·84	1·09	32·69			
$S(s^2p^3d^1)\ ^5D$	0·74	0·88	10·34	0·81	1·01	35·04	3·36	4·01	2·06
$S(s^1p^4d^1)\ ^5F$	0·72	0·87	10·49	0·81	1·01	35·57	3·05	3·85	2·45
$S(s^1p^3d^2)\ ^7F$	0·72	0·86	10·53	0·81	0·98	36·43	1·18	1·89	5·92
$Si(s^2p^1d^1)\ ^3F$	0·93	1·12	7·30	1·10	1·38	19·75	2·71	3·68	1·03
$Si(s^1p^2d^1)\ ^5F$	0·93	1·10	7·37	1·10	1·30	20·82	2·37	3·33	1·26
$Si(s^1pd^2)\ ^5G$	0·93	1·07	7·53	1·02	1·19	23·10	1·70	2·44	2·03
$P(s^2p^2d^1)\ ^4F$	0·81	0·98	8·80	0·93	1·15	27·36	3·20	3·87	1·42

Hartree-Field

$S(s^2p^4)$	0·76	0·93	10·70	0·93	1·24	31·40	-	-	-
$S(s^2p^2d^2)$	0·76	0·89	11·26	0·85	1·04	37·28	2·36	3·09	2·30
$S(s^1p^3d^2)$	0·76	0·88	11·39	0·85	1·02	37·90	2·36	3·02	2·53

The 2p orbital of $S(sp^3d^2)\ ^7F$ has A = 128.74 .

A comparison between the position of the principle maxima of the 3s,3p,and 3d orbitals, their mean radii,and initial slopes for a variety of configurations of sulphur together with the other elements of interest to us here,may be obtained from Table 6. In this all the pertinent data is to view. There is nothing untoward about the shape of the 3s and 3p orbitals. For this reason nearly all of the figures refer only to the 3d orbital. Figure 7 however illustrates the 3s and 3p orbitals of $S(s^2p^4)\ ^3P$.

It is interesting to observe that for $S(sp^3d^2)^7F$ the radial maxima of the valence orbitals, which lie at 0.72 Å, 0.81Å and 1.18 Å,for the 3s,3p and 3d orbitals respectively, are all well within the S-F distance in SF_6. This is the opposite of the view maintained up to the present time,as noted in Chapter I,that the 3d orbital is highly diffuse. Indeed the need for the theory of ligand contraction with regard to orbital size is entirely removed by this result[85]. Craig and Thirunamachandran[85], together with Bendazzoli and Zauli[86] have since defended the contraction theory. Their calculations are however for a valence state based

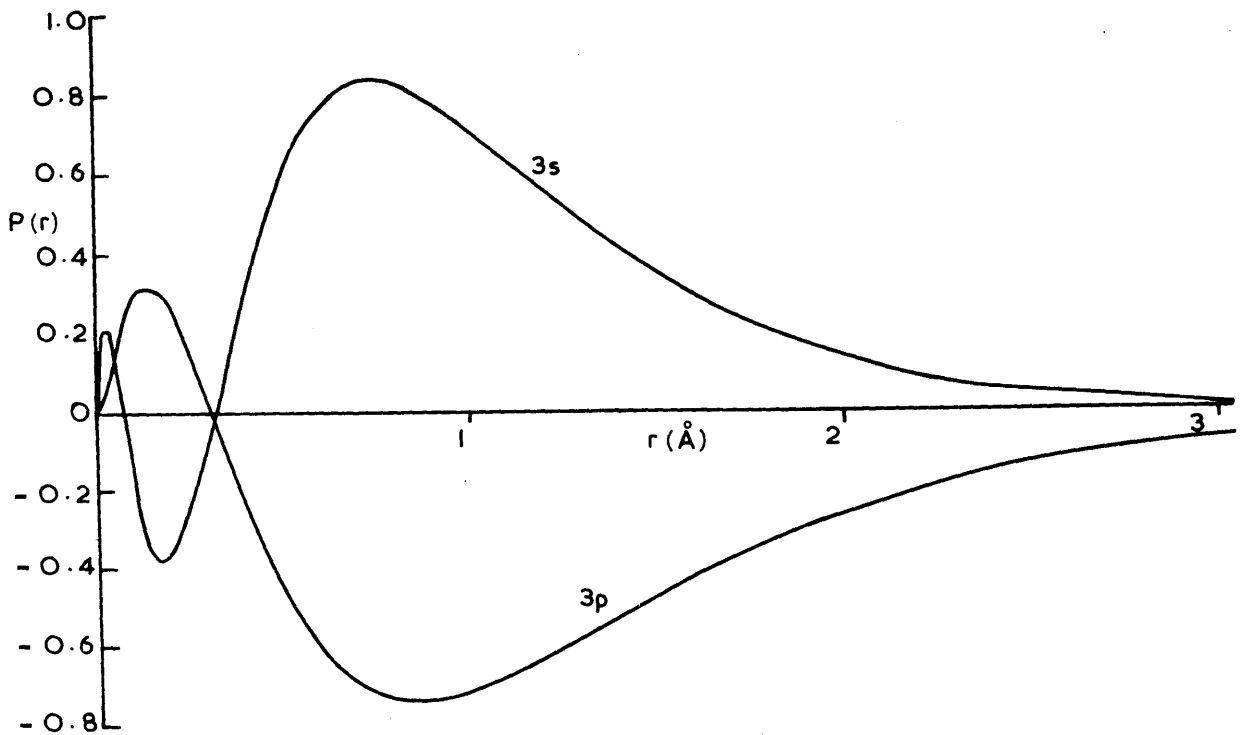


Fig. 7. Hartree-Fock wave functions for the 3s and 3p orbitals of $S(s^2p^4)\ ^3P$.

solely on an sp^3d^2 configuration of sulphur. It has since been shown, as just mentioned, that when a more realistic basis of equivalent hybridised orbitals is taken, the ^7F term and the valence state 3d orbital are very similar in size.

This leads us to another point raised in Chapter I. How accurately is a 3d orbital represented by a Slater orbital? The answer to this question is the substance of Figure 8. In this the ^7F term of sp^3d^2 is again traced and is to be compared with the curves labelled B and C. The former is for a Slater orbital. This one may recall has the form $r^3.\exp(-Z_{eff}/n\ .r)$, with $Z_{eff}(3d) = 1.65$, the value obtained on applying Slater's rules to $S(sp^3d^2)$. It has a mean radius of 3.36 Å. Curve C is for a Slater orbital having the same mean radius as that of $S(sp^3d^2)\ ^7F$, 1.88 Å and hence $Z_{eff}(3d) = 2.95$.

It is clear that the Slater orbital for $S(sp^3d^2)$ bears no resemblance at all to the self consistent field orbital, whilst even if the effective nuclear charge is chosen to obtain the best match, the representation of the orbital by a single exponential function, although improved, is inadequate. Craig and Thirunamachandran have

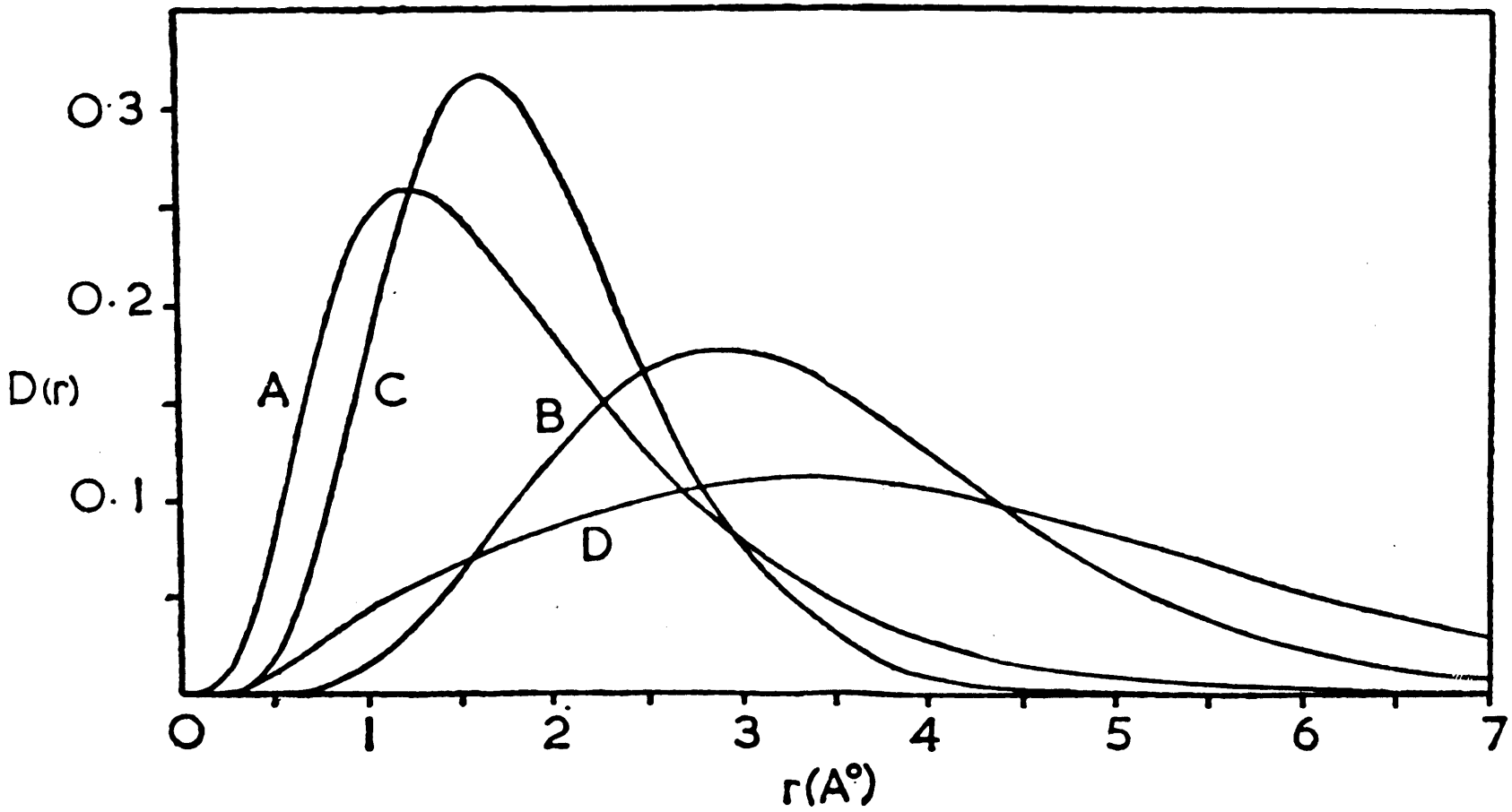


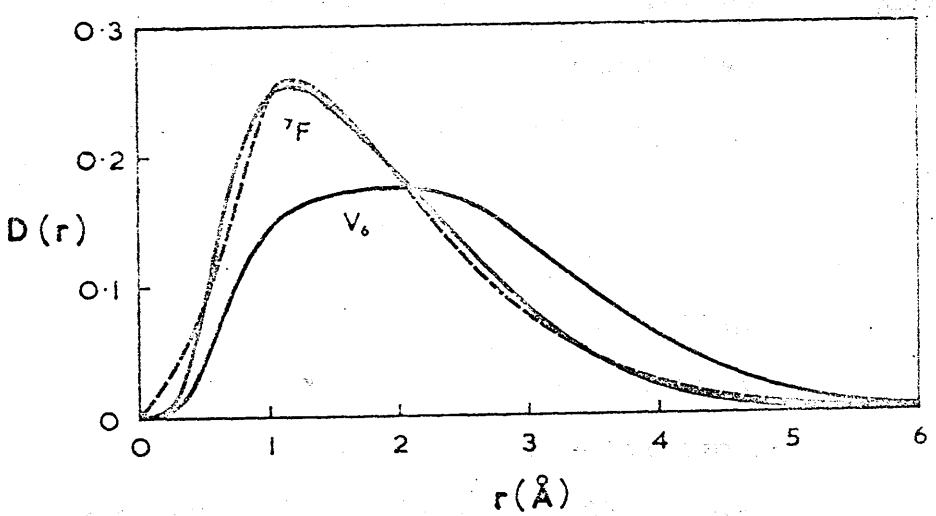
Fig. 8. Radial functions D(r) for the 3d orbital of sulphur $S(sp^3d^2)$ ^7F -- A, $S(s^2p^3d^1)$ ^5D -- D. Curves B and C are analytic functions with single exponents of 0.61 and 0.98.

in their work used a double exponential function for the 3d orbital and obtain a close correspondance with the self consistent field function for $S(sp^3d^2)$ ^7F and $S(s^2p^3d^1)$ ^5D, which is also shown again in this figure as curve D. A double exponential function has the form $r^3(C_1.e^{-k_1 r} + C_2.e^{-k_2 r})$ where their are now two orbitals exponents k_1 and k_2 to be determined together with a coefficient of mixing C_1.

Figure 9 shows the 3d orbital for ^7F term and the analytic function of Craig and Thirunamachandran. The former is the dotted curve. Clearly two exponentials are far better than one. Also to be seen is the curve for the valence state based solely on an sp^3d^2 configuration of sulphur. The use of a double exponential representation for a 3d orbital and indeed a multi-exponential representation for an orbital if necessary, is urged in an early paper of Slater[87]. More recently it has been found that the analytic self consistent field functions of Watson for the 3d orbitals of the transition metals may be quite accurately traced by a double exponential function[88].

Although the septet term of $S(sp^3d^2)$ is the

Fig. 9. The Hartree-Fock wave function of $S(sp^3d^2)\ ^7F$ as approximated by a double exponential function, dotted curve, by Craig and Thirunamachandran. V_6 is a particular valence state orbital.



most favourable amongst the second row elements for exhibiting the effect of exchange upon the shape of the 3d orbital, this behaviour is not restricted to sulphur. Figure 10 depicts some 3d orbitals for d^1 and d^2 configurations of Silicon. Here again the 3d orbital of $Si(sp^2d)$ ^5F, curve a, and $Si(s^2pd)$ ^3F, curve b, are similar and highly diffuse. The mean radii are 3.68 Å for the former and 3.33 Å in the latter case. In contrast the 3d orbital of $Si(spd^2)$ ^5G, curve c, is far more compact, having a mean radius of 2.44 Å, which is to be compared with 3.18 Å for the Hartree solution of $Si(spd^2)$, curve d, As is to be expected the difference between these two orbitals is less than in the case of sulphur but the distinction between them is still quite marked. This is also reflected in the value of A for the two orbitals, which increases from 1.04 to 2.03 on the inclusion of exchange.

Figure 11 shows a similar behaviour for phosphorus. The 3d orbital for $P(s^2p^2d^1)$ ^4F, curve a, is highly diffuse even compared with the Hartree 3d orbital of $P(sp^2d^2)$, curve b. Also to be seen are some very interesting Hartree orbitals

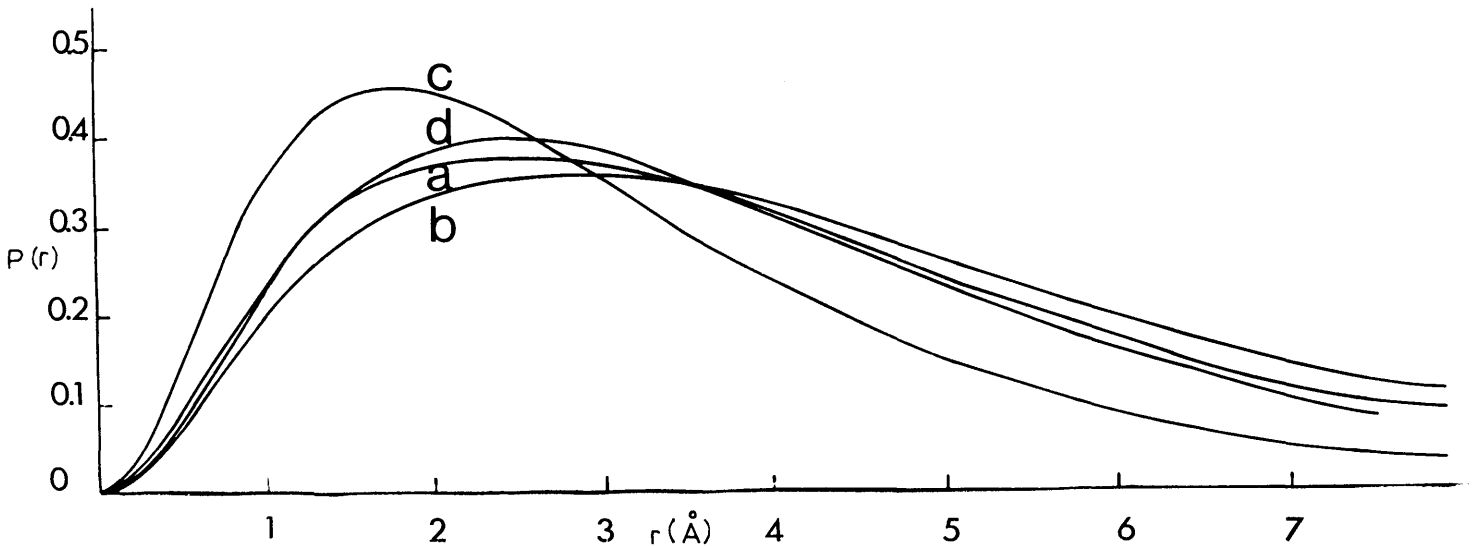


Fig. 10. Self consistent field functions P(r) for Si(sp^2d) ^5F -- a, Si(s^2pd) ^3F -- b, Si(spd^2) ^5G -- c and Si(spd^2) -- d.

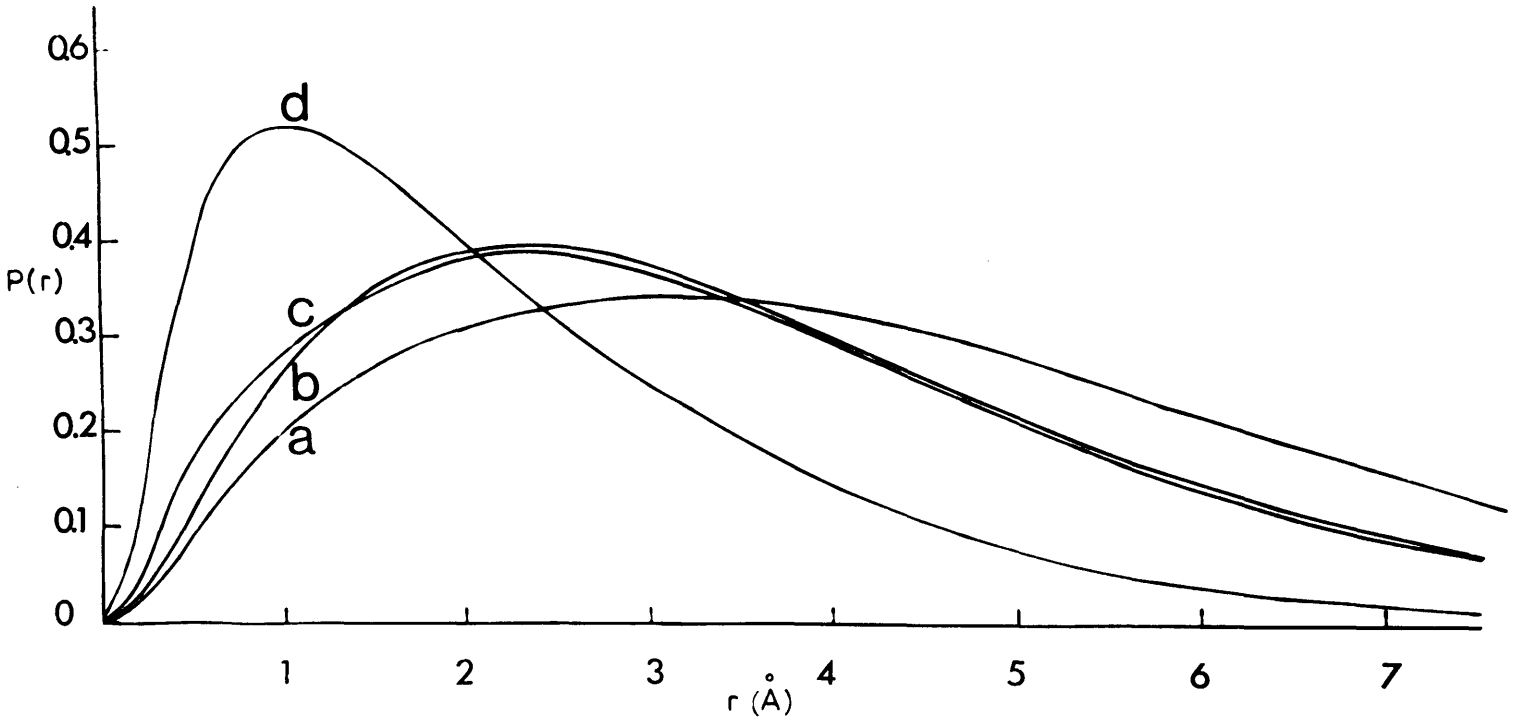


Fig. 11. Self consistent field functions for $P(s^2p^2d)\ ^4F$ --a, $P(sp^2d^2)$ -- b, $Ar(sp^5d^2)$ -- c, $Ar(sp^3d^4)$ -- d.

for argon. The 3d orbital of $Ar(sp^5d^2)$, curve c, is almost identical to that of $P(sp^2d^2)$, their mean radii differ by but 0.17 Å. Indeed the Hartree 3d orbitals for the series $Si(spd^2)$ to $Ar(sp^5d^2)$ are all very similar and only a gradual increase in the initial slopes on moving across the period distinguishes them. This may be seen at a glance in Table 6. For the configuration $Ar(sp^3d^4)$ the 3d orbital is quite compact with the radial maximum lying at 1.02 Å, curve d. It so stands out in sharp relief against the 3d orbital of $Ar(sp^5d^2)$ for which r_{max} is 2.36 Å.

To complete this series of illustrations let us return to sulphur. In Figure 12 the Hartree 3d orbitals of $S(sp^3d^2)$, curve a, and $S(s^2p^2d^2)$, curve b, which are scarcely separable, are placed in perspective against the 3d orbitals of the singly positive ions $S^+(sp^3d)$, curve c, and $S^+(sp^2d^2)$, curve d. Clearly the acquistion of a positive charge results in a considerable contraction of the orbital. Further, if one may also retain a d^2 configuration then the most compact 3d orbital of all considered here is obtained. The mean radii falls from 3.02 Å to 2.05 Å on the ionisation of the d electron from $S(sp^3d^2) \rightarrow S^+(sp^3d^1)$. For the ionisation of

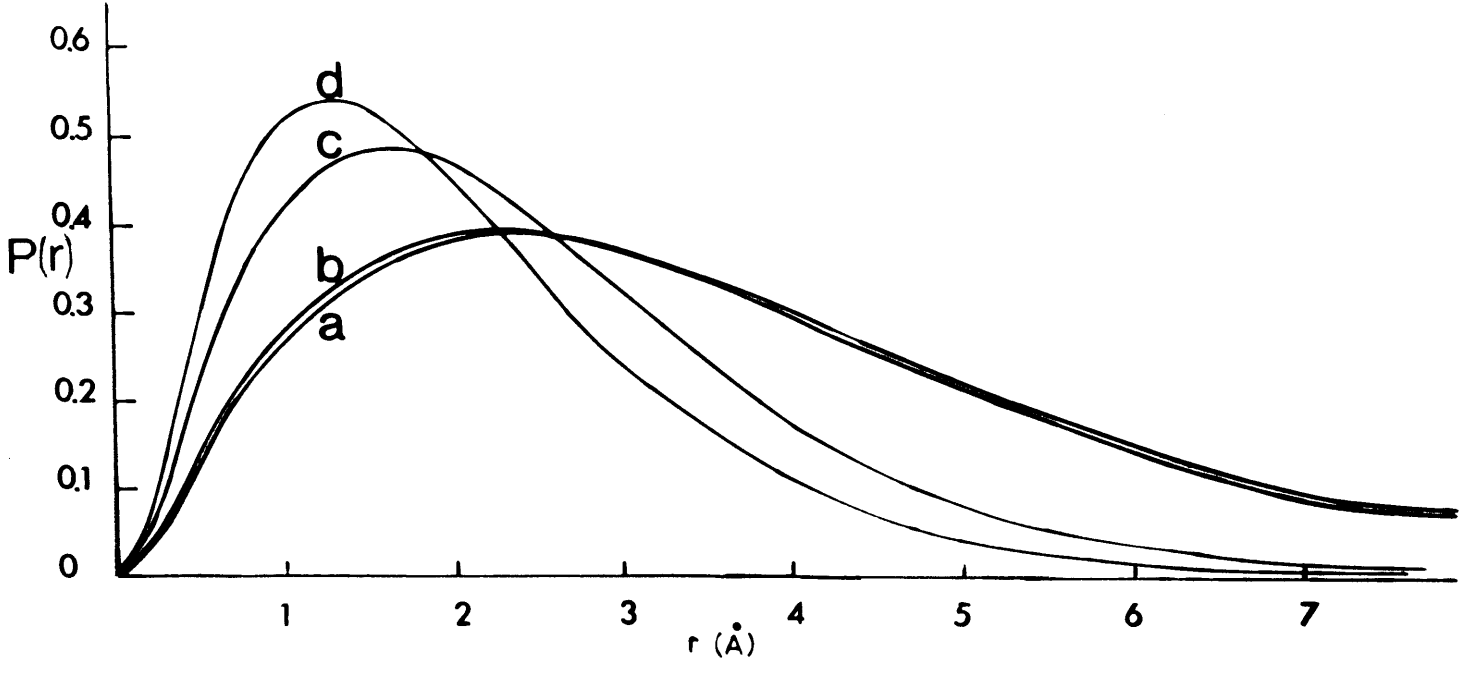


Fig. 12. Hartree self consistent field functions for $S(sp^3d^2)$ -- a, $S(s^2p^2d^2)$ -- b, $S^+(sp^3d)$ -- c, $S^+(sp^2d^2)$ -- d.

$S(s^2p^2d^2) \rightarrow S^+(sp^2d^2)$ the change is even more spectacular $\bar{r}$ passing from 3.09 Å to 1.69 Å.

Apart from Hartree and Hartree-Fock wave functions, Hartree-Fock-Slater wave functions have also been calculated for a variety of sulphur configurations. Table 6 permits a comparison to be made between these methods. The free electron approximation has quite evidently overestimated the exchange terms, and produced orbitals which are deceptively compact. Nevertheless two results deserve mention since they are not duplicated by other methods.

The first pertains to $S^{2+}(sp^2d^1)$. This shows a continuation of the trend noted in Figure 12, with the 3d orbital becoming more compact as the sulphur atom increases its positive charge. With the successive ionisation of the p electron as $S(sp^4d) \rightarrow S^+(sp^3d) \rightarrow S^{2+}(sp^2d)$ the position of the maximum of the 3d orbital moves towards the nucleus, r_{max} changing from 1.37 Å through 1.01 Å, to 0.89 Å. The initial slope of the function increases quite sharply as is reflected in the values of A which are 4.80, 9.49 and 12.68 for the three configurations respectively.

The second result to note is that for

$S(s^1 3p^3 3d^1 4s^1)$. Here the 3d orbital is no longer an outer orbital, but an inner orbital. The distinction is quite palpable. The maximum of the 3d orbital lies at 1.01 Å although as has been shown d^1 configurations are usually highly diffuse. For $S(s^2p^3d^1)$, r_{max} = 2.84 Å in the Hartree-Fock-Slater approximation its imitial slope is quite high, A being 9.12 as compared with 4.34 for $S(s^2p^3d)$. Indeed the outer 4s electron has little influence on the inner electrons and the 3d electron effectively experiences the field of a positively charged sulphur atom. That this is the case, is shown by the close resemblance of the 3d orbital for $S(sp^3d^1 4s^1)$ to that of $S^+(sp^3d^1)$.

Contours of ψ for an Octahedral Hybrid Orbital

In Chapter I, Figure 2, an octahedral hybrid orbital ψ was plotted on the assumption that the radial wave functions of the 3s, 3p and 3d orbitals are equal. With the acquisition of the radial wave functions for $S(sp^3d^2)\ ^7F$ it is now possible to lift this restriction and to construct more realistic contours for an octahedral hybrid.

$$\psi_{+z} = \frac{1}{\sqrt{6}} (s + \sqrt{3}p_z + \sqrt{2}d_{z^2})$$

where $s = \sqrt{\frac{1}{4\pi}} \cdot \frac{P(3s;r)}{r}$

$p_z = \sqrt{\frac{3}{4\pi}} \cdot \cos\theta \cdot \frac{P(3p;r)}{r}$

and $d_{z^2} = \sqrt{\frac{5}{16\pi}} \cdot (3\cos^2\theta - 1) \cdot \frac{P(3d;r)}{r}$

For a given value of ψ,θ is determined over a range of values for r. The resulting contours are illustrated by the polar diagram,which is Figure 13. By rotating the contours about the bond axis, the complete contours may be visualised.

Although the intricate nodal system is interesting the most eyecatching feature is the manner in which the contours rise to a peak at 0.59 Å. This is very close to the centre of an S - F bond. The sp^3d^2 hybrid orbital would therefore appear to be excellently disposed for overlapping with a suitable ligand orbital,although it must of course be remembered that these contours will be considerably perturbed,if a fluorine atom,for example were to be placed at 1.5 Å.

Conclusion

The 3d orbital of the second row atoms Si, P, S, Cl, and Ar. has been found to be highly diffuse for the neutral elements in d^1 configurations. When the 3d orbitals are doubly

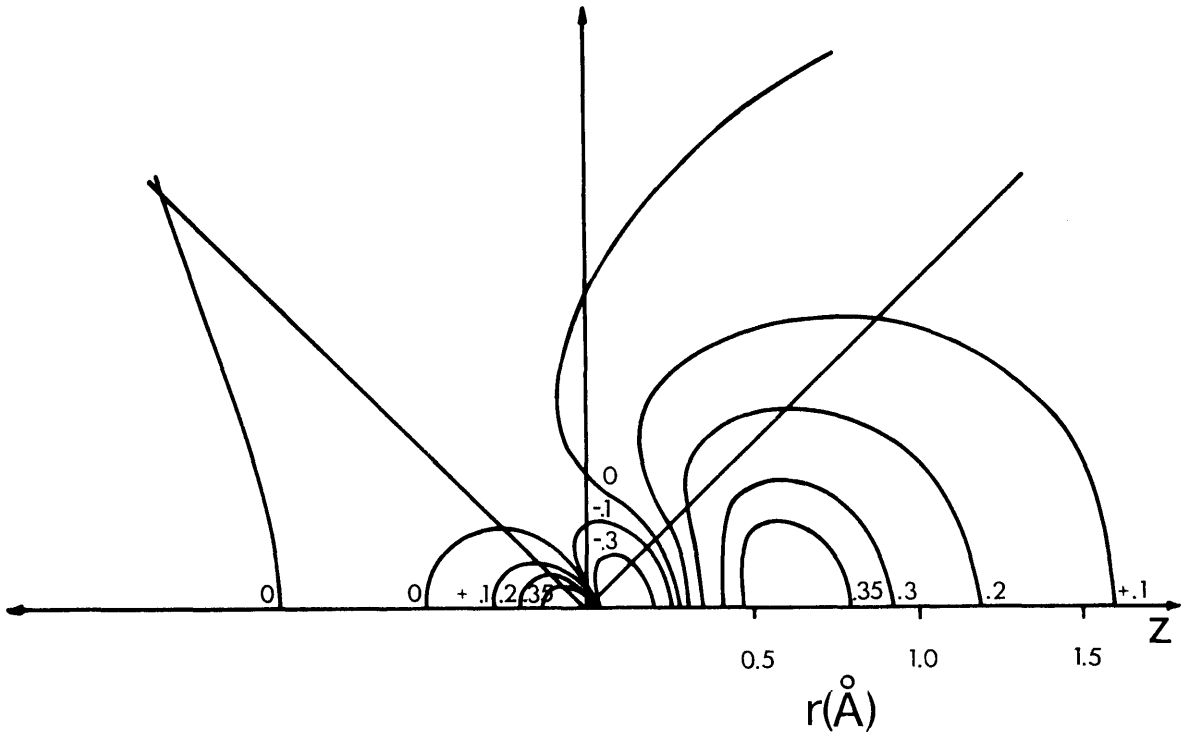


Fig. 13. Contours of an octahedral hybrid orbital of sulphur suitable for bond formation in the z direction.

occupied the nuclear screening decreases and the orbital quite naturally contracts. What is rather astonishing is the observation that on allowing partially for the correllation of the electrons, through the intermediary of the Fermi hole, the 3d electrons are forced to move through so great a distance towards the nucleus. The chemical implication is clear. If the size of the free atom orbital ia a dominant factor in bond formation, then for atomic d^2 configurations the 3d orbital of the elements of the second row under review could participate quite readily in molecular binding. If the atom is positively charged the 3d orbital is, as is to be expected, quite compact and again suitable with respect to size for bonding purposes. Nevertheless, having reached this optimistic highspot our attention must inevitably turn to the energetics involved.

CHAPTER V

A Question of Energetics

The key figure in the early development of the concept of energy is Christiaan Huygens, a man whose interests ranged from games of chance to the properties of gunpowder.

D. W. Theobald 1966

Introduction

It is now intended to interweave two important topics; the energies of the configurations which have been mentioned in the preceeding pages and the one electron orbital energies ε_{nl}. The link between them will be provided by Koopmans theorem. Let us begin by considering the configurational energies and see how they lie with respect to the energy of the ground state.

Configurational Energies and Promotion Energies

In Table 7 the energies of configurations for Si, P, S, Cl and Ar are listed. Both Hartree and Hartree-Fock energies, in Rydbergs, are given

Table 7

Configuration energies (Rydbergs) and promotion energies (eV)

	Hartree		Hartree-Fock		Experimental	
	E	ΔE	E	ΔE	ΔE	$\Delta E^{est.}$
$S(s^2p^4)\ ^3P$	784•82	-	795•01	-	-	-
$S(s^2p^3d^1)\ ^5D$	-	-	794•48	7•21	8•42	> 7•3
$S(s^2p^4d^2)$	784•03	10•74	-	-		
$S(s^1p^4d^1)\ ^5F$	-	-	793•67	18•22		
$S(s^1p^3d^2)\ ^7F$	783•30	20•67	793•21	24•48		>31•3
$S^+(s^1p^3d^1)$	782•75	28•15	-	-		
$S^+(s^1p^2d^2)$	781•83	40•66	-	-		
$Cl(s^2p^5)$	907•48		-	-		
$Cl(s^1p^4d^2)$	905•57	25•98	-	-		
$Ar(s^2p^6)$	1041•06		-	-		
$Ar(s^1p^5d^2)$	1038•54	34•27	-	-		
$Ar(s^1p^3d^4)$	1037•33	50•73	-	-		
$Si(s^2p^2)\ ^3P$	570•05	-	577•71			
$Si(s^2p^1d^1)\ ^3F$	-	-	577•22	6•66	6•20	6•35

Table 7 (cont'd)

	Hartree		Hartree-Fock		Experimental	
	E	ΔE	E	ΔE	ΔE	$\Delta E^{est.}$
$Si(s^1p^2d^1)\ ^5F$	-	-	577•03	9•25		13•42
$Si(s^1p^1d^2)\ ^5G$	568•98	14•55	576•76	12•92		23•88
$P(s^2p^3)\ ^4S$	672•46	-	681•44	-		
$P(s^2p^2d^1)\ ^4F$	-	-	680•85	8•02	8•71(^2F)	9•17
$P(s^1p^2d^2)$	671•23	16•73	-	-		35•76

and the promotion energy ΔE in electron volts. The last column contains where observed, the value of ΔE as obtained from spectroscopic data[46], together with other authors estimates. At this juncture it might well be pointed out that the omissions in this Table and Table 5 for d^1 configurations in the Hartree field are due to the fact that it was not possible to find a solution of the self consistent field equations. In these cases after very few iterations from a variety of initial estimates, the d electron became unbound. Similarly no solutions were found in the Hartree-Fock-Slater field for d^2 configurations of sulphur due to the onset of oscillatory behaviour during the iteration process.

Looking firstly at the configurations of Silicon, the agreement between the Hartree-Fock promotion energy for $Si(s^2p^2)\ ^3P \rightarrow Si(s^2p^1d^1)\ ^3F$ and the observed value allows one to have a little confidence that the other results presented might be of the right order of magnitude. Both $Si(sp^2d^1)\ ^5F$ and $Si(spd^2)\ ^5G$ lie above the ionisation limit, which is 8.15 e.v., $Si(s^2p^2) \rightarrow Si^+(s^2p^1)$ Jordan's estimates [89] of ΔE appear to be widely astray in this instance. A similar pattern is portrayed for

phosphorus where again Jordan's estimate for ΔE to the d^2 configuration seems out of proportion.

On reaching sulphur the difference between the calculated and observed promotion energies for $S(s^2p^4) \rightarrow S(sp^3d^1)\ ^5D$ has increased but the two values are still comparable. Whereas with silicon the promotion energy calculated within the Hartree approximation exceeded that obtained by the Hartree-Fock method, in the case of sulphur this situation is reversed consequently the promotion energies to the positive ions $S^+(sp^3d^1)$ and $S^+(sp^2d^2)$, which are given for the Hartree field, probably represent lower limits. The promotion energy to $S(sp^3d^2)$ of 24.48 e.v. is below the quoted estimate of Bendazzoli and Zauli[86] but may be compared with the value of 24.8 e.v. calculated by Craig and Zauli[28]. For chlorine and argon the promotion energy to a d^2 configuration increases quite markedly, whilst the formation of a compound, based principally on $Ar(sp^3d^4)$ which lies 50.73 e.v. above the ground state seems most unlikely.

It would so appear that for a second row element to attain a configuration in which the 3d orbital is of a suitable size for bonding requires a considerable amount of energy. Further such

conditions are more readily attainable to the left of the period than the right. On this basis, it is therefore perhaps not so surprising that $[AlF_6]^{3-}$, $[SiF_6]^{2-}$ are well known species whilst ClF_7 and ArF_8 have as yet to be prepared.

Koopmans Theorem

From chapter II it may be recalled that the energy E of an atom possessing i electrons, within the Hartree approximation is given by the expression

$$E = \sum_i I(n_i l_i) + \frac{1}{2}\sum_{ij} F_o(n_i l_i; n_j l_j)$$

If the k^{th} electron is ionised adiabatically, the energy E^+ of the resultant ion is of the form

$$E^+ = \sum_{i \neq k} I(n_i l_i) + \frac{1}{2}\sum_{ij \neq k} F_o(n_i l_i; n_j l_j)$$

The ionisation potential P_k is defined by the difference $E^+ - E$. Hence

$$P_k = E^+ - E = -[I(n_k, l_k) + \sum_{i \neq k} F_o(n_i l_i; n_k l_k)]$$

On consideration of the s.c.f. equation for the orbital, k, $P(n_k l_k; r)$

$$\left[\frac{d^2}{dr^2} + \frac{2Y(n_k l_k; r)}{r} - \frac{l(l+1)}{r^2}\right] P(n_k l_k; r) = \varepsilon_k . P(n_k l_k; r)$$

it may be seen that $P_k = -\varepsilon_k$. That is, assuming the wave functions remain unaltered on ionisation, the ionisation potential for an electron in a particular orbitalmay be identified with the negative of the one electron energy for that orbital. Koopmans

first demonstrated this fact in 1933,for Hartree-Fock wave functions[90]. When one considers the removal of the d electron from a d^1 configuration of sulphur Koopmans theorem is indeed applicable,for all inner wave functions are scarcely affected by the process. The ionisation potential as determined by the energy difference $E(S^+, s^2p^3, {}^4S)-E(S, s^2p^3d, {}^5D)$ allows for reorganisation on ionisation. It is 1.82e.v. whilst the value as obtained from the one electron orbital energy is 1.77 e.v. From spectroscopic data the observed ionisation potential is 1.94 e.v. which should be compared with the former of the two calculated values. The latter is for an adiabatic process,as is involved in an electron impact measurement. Since little reorganisation takes place on the loss of the electron the difference between the two calculated ionisation potentials is here not very great.

When one considers the d^1 configurations of Si a different pattern emerges. There is a degree of reorganisation on the ionisation $Si(s^2p^1d^1) \rightarrow Si^+(s^2p^1)$ as is reflected in the change of ε_{3p} from 11.47 e.v. to 15.94 e.v. on the removal of the d electron. Now, the energy difference

Table 8

Orbital energies (eV)

	3s			3p			3d		
	ϵ^{H}	ϵ^{HPS}	ϵ^{HF}	ϵ^{H}	ϵ^{HPS}	ϵ^{HF}	ϵ^{H}	ϵ^{HPS}	ϵ^{HF}
$S(s^2p^4)$	19•39	20•80	23•92	8•25	10•28	11•90	–	–	–
$S(s^2p^3d^1)$	–	25•80	29•21	–	14•76	19•03	–	1•85	1•77
$S(s^1p^4d^1)$	–	26•12	34•57	–	15•03	17•94	–	1•89	1•74
$S(s^1p^3d^2)$	29•38	–	35•48	17•77	–	20•58	2•26	–	3•32
$S(s^1p^3d^1s^1)$	–	29•05	–	–	17•67	–	–	2•92	(4s 3•93)
$S^{+}(s^1p^3d^1)$	33•34	34•55	–	21•76	23•19	–	7•12	8•47	–
$S^{+}(s^1p^2d^2)$	35•14	36•10	–	23•41	24•58	–	8•36	9•26	–
$S^{2+}(s^1p^2d^1)$	–	45•85	–	–	44•78	–	–	18•09	–
$Si(s^2p^1d^1)$	–		18•19	–		11•47	–		1•86
$Si(s^1p^2d^1)$	–		22•05	–		12•90	–		2•09
$Si(s^1p^1d^2)$	20•27		27•27	11•98		19•89	2•24		2•89
$P(s^2p^2d^1)$	–		23•56	–		15•36	–		1•88
$P(s^1p^2d^2)$	24•71		–	14•79		–	2•26		–
$Cl(s^1p^4d^2)$	34•25		–	20•93		–	2•26		–
$Ar(s^1p^5d^2)$	39•34		–	24•26		–	2•25		–
$Ar(s^1p^3d^4)$	40•85		–	25•51		–	3•28		–

$E(Si^+ s^2p^1\ ^3P) - E(Si\ s^2p^1d^1\ ^3F)$ of 1.01 e.v. differs quite markedly from the 3d orbital energy of 1.86 e.v. The observed spectroscopic ionisation potential is 1.95 e.v. It may well be that there is some configuration interaction also taking place, as has been investigated recently in the case of magnesium[91].

When d^2 configurations are considered the situation is even more marked and is probably entirely due to the large amount of reorganisation which occurs on ionisation. As may be seen from Table 7, in the Hartree field for sulphur, $E(S^+\ sp^3d^1) - E(S\ sp^3d^2)$ is 7.48 e.v. whilst ε_{3d} for the 3d orbital of $S(sp^3d^2)$ is but 2.26 e.v. Even the 3p orbital is quite affected; $E(S^+\ spd^2) - E(S\ sp^3d^2)$ is 19.99 e.v. as compared with a 3p orbital energy of 17.77 e.v. Clearly the identification of the d orbital energy with a spectroscopic ionisation potential would be quite erroneous for a d^2 configuration.

The Valence Orbital Energies

The energies of the valence orbitals of the second row elements under review are collated in Table 8. In passing, one may note that in nearly all

the example$ given the energies as obtained by Hartree, Hartree-Fock-Slater and Hartree-Fock methods decrease in that order, as is to be expected. Two features of this table deserve careful elaboration. It is to be seen that energetically, a 3d orbital of a second row element is quite different from a 3s or 3p orbital. Even for $S(sp^3d^2)\ ^7F$, where the 3d orbital is compact, the orbital energy is very small, 3.32e.v., although as has just been demonstrated this does not necessarily imply that it is very loosely bound. The 3s and 3p orbitals, are very much higher in energy, being 35.48 e.v. and 20.58 e.v. respectively. Further, on passing across the period, the d orbital energy is almost independant of the atomic number, as is displayed by the Hartree d^2 configurations $Si(spd^2)$ to $Ar(sp^5d^2)$

This marked difference in character between the 3d and other valence electrons has its origin in their respective effective potential energies V_{eff}. To confirm this I made a study of the effective potential energy within the Hartree approximation, for the valence electrons of the d^2 sequence just mentioned. The effective

Table 9

The position and magnitude of the minimum in the effective potential energy for the 3p and 3d electrons of Si, P, S, Cl and Ar.

		$\underline{r}$ (Å)	$-V_{eff}^{min}$ (e.v.)
Si	3p	0.090	464.67
	3d	0.933	5.57
P	3p	0.080	565.44
	3d	0.678	7.57
S	3p	0.074	676.81
	3d	0.551	10.74
Cl	3p	0.069	798.40
	3d	0.466	15.11
Ar	3p	0.064	927.52
	3d	0.403	20.62

potential V_{eff} is given by the expression

$$V_{eff} = -[\frac{2}{r} Y(nl;r) - \frac{l(l+1)}{r^2}]$$

This function is illustrated in Figure 14 for the valence electrons of $S(sp^3d^2)$. A striking constrast in behaviour is to be seen when l increases from 1 to 2. For the 3p electrons the minimum of V_{eff} is - 676.81 e.v. and lies at r=0.07 Å. The minimum energy for the 3d electron is only 10.74e.v. and is located at 0.55 Å.

Clearly,for the 3d electron the centrifugal term $l(l+1) / r^2$,counterbalances the potential generated by the other fifteen electrons over a very wide range of r. As a consequence d^2P / dr^2 is much smaller for the 3d electrons than for the 3s or 3p and the Hartree equation for the 3d electron must inevitably produce an orbit with an extremely long tail and of a low energy.

A similar pattern is common to the other elements mentioned,as is to be seen from Table 9. This lists the minima of V_{eff} for the 3p and 3d electrons,together with the value of r at which they occur. There is a slight increase in the binding of the d electrons on passing from Si to Ar, as may be observed in Figure 15. Although there is a

Fig. 14. The effective potential energy for the valence electrons of $S(sp^3d^2)$.

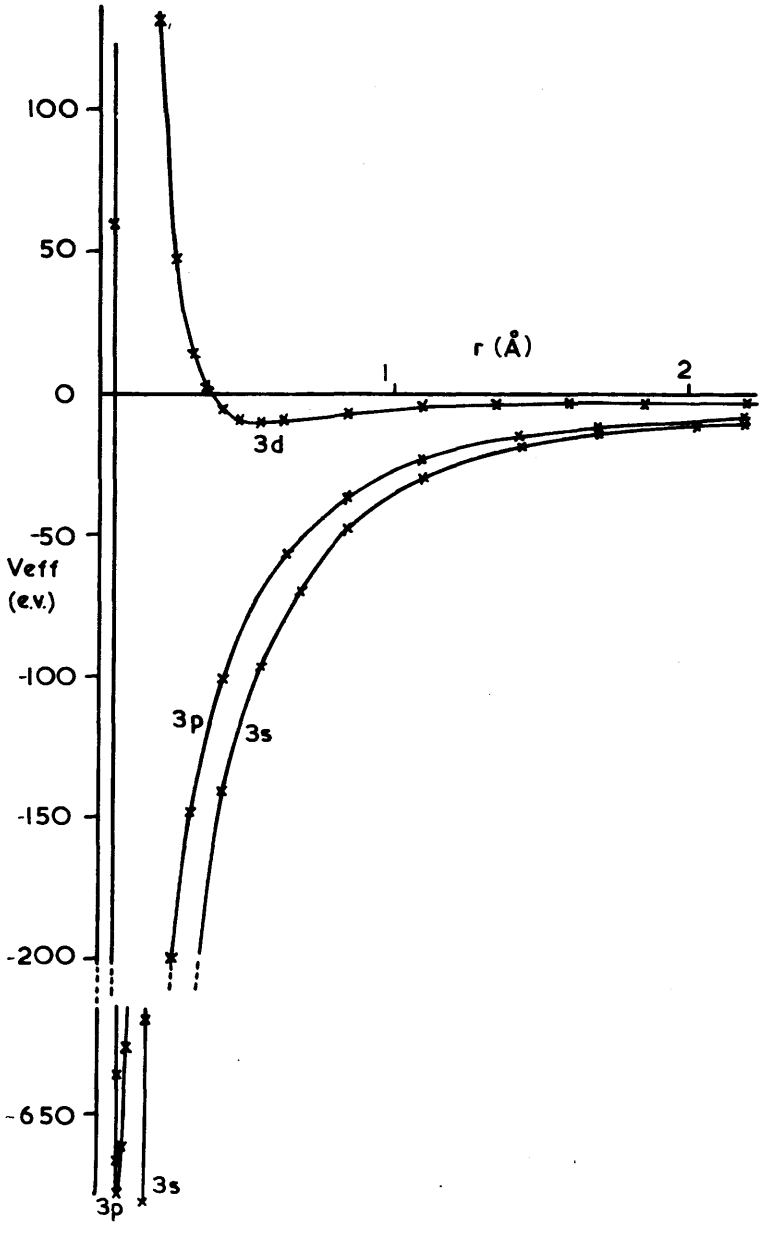


Fig. 15. The effective potential energy for the 3d electrons of Si(spd^2), S(sp^3d^2) and Ar(sp^5d^2).

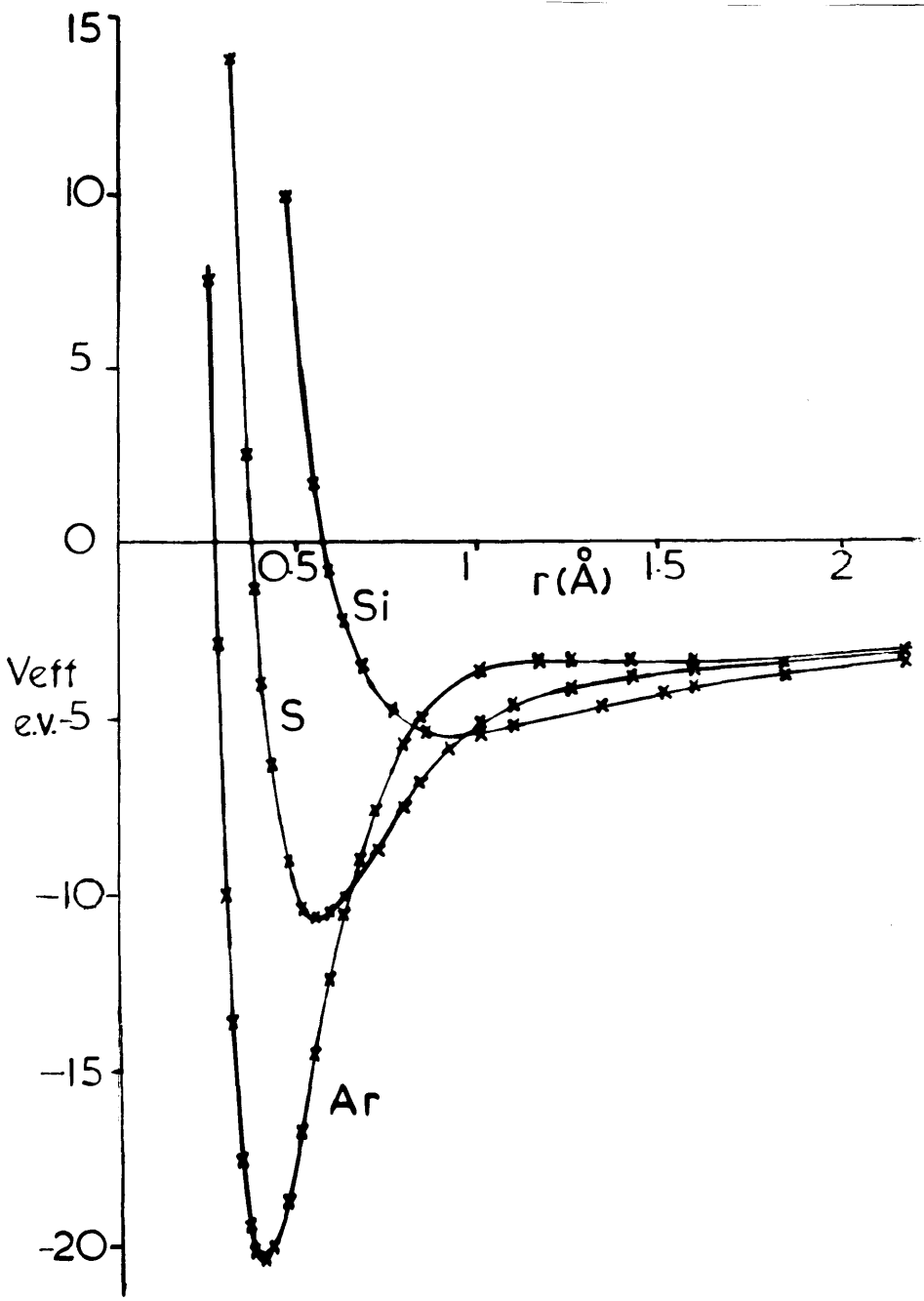


Table 10

	$-V_{nucleus}$			$V_{electrons}$			K			$-\epsilon$		
	s	p	d	s	p	d	s	p	d	s	p	d
Si	252•40	207•70	81•06	181•78	158•58	73•0	50•35	37•14	5•82	20•27	11•98	2•24
P	307•79	257•24	92•35	217•35	193•19	83•31	65•73	49•26	6•78	24•71	14•79	2•26
S	366•66	310•55	102•42	254•86	229•93	92•60	82•42	62•85	7•56	29•38	17•77	2•26
Cl	429•24	367•62	111•28	294•47	268•85	100•87	100•52	77•84	8•15	34•25	20•93	2•26
Ar	495•60	428•69	118•86	336•37	310•18	108•07	119•89	94•25	8•54	39•34	24•26	2•25

gradual increase in depth of the minima, the influence of this on the final wave function is small. As has been seen in the preceeding chapter there is but a gradual rise in the initial slope of the Hartree 3d function for d^2 configurations on passing across the period.

Figure 16 is reproduced from Slater's Theory of Atomic Structure Volume I [64] and shows that the 3d electron of the second row elements considered here is very similar to such an electron attached to K^+ but quite different from the 3d electron of the transition metal ion Cu^+. For these two ions V_{eff} has a minimum of 8.16 e.v. and 134.64ev. respectively.

A Partition of the Orbital Energy

For a particular electron, the orbital energy may be decomposed into three constituents. These are the potential energy afforded by the nucleus, $V_{nucleus}$, the potential energy due to the other electrons $V_{electron}$ and the kinetic energy, K

$$-\varepsilon = -V_{nucleus} + V_{electron} + K$$

Such a partition for the valence electron of the Si - Ar sequence is quite illuminating and is contained in Table 10.

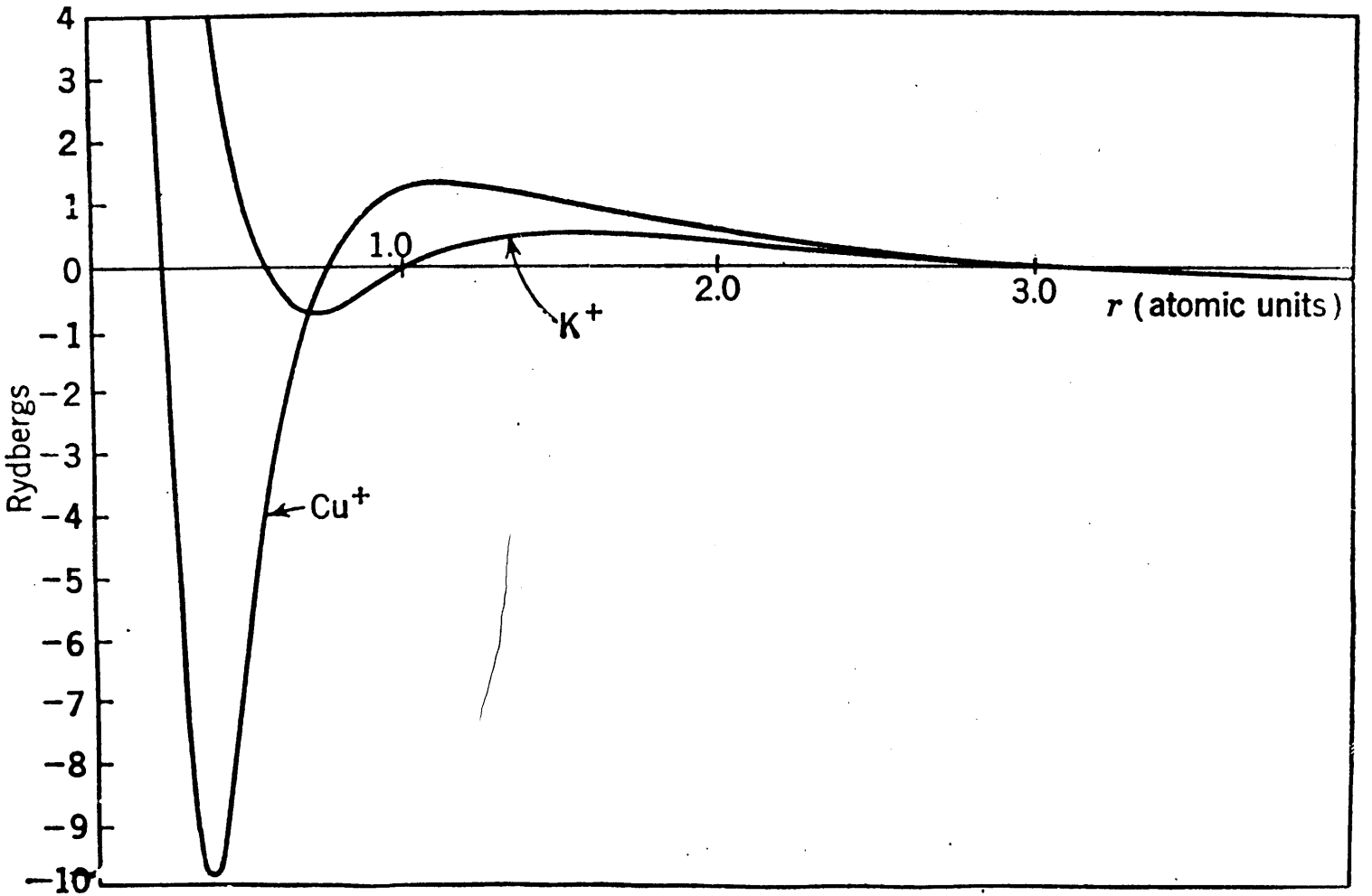


Fig. 16. The effective potential energy for a 3d electron of K^+ and Cu^+.

The link between the valence electrons via their principal quantum number is clearly very weak, the 3d electron assuming the role of an outsider. In each case the 3d electrons behave as if they were restricted to move on the periphery of a closed shell, experiencing thereby a nuclear charge of +2. Indeed one may note that the orbital energy is just of the magnitude expected for such a situation. On assuming hydrogenic orbitals one may readily obtain the relation

$$2Z^2(3d) / n^2 = 2\varepsilon(3d) + F_o(3d,3d)$$

where the coulomb integral $F_o(3d,3d)=0.5162\ Z(3d)/3$ Rydbergs; whence if each d electron screens the other by 0.33, $Z(3d) = 1.67$ and the orbital energy $\varepsilon(3d)$ is 2.26 e.v.

Conclusion

For the second row elements under review, it is quite plain that a considerable quantity of energy is required for the element to attain a configuration in which the 3d orbital is of a suitable size for bonding purposes. Even when such a configuration has been reached, there is a gross disparity between the energies of the valence orbitals for the neutral atoms.

As is to be seen in Table 8 this situation may be ameliorated by the acquistion of positive charge. At the same time, the ligands of a molecule would acquire some negative charge. In this context it is perhaps pertinent to note that energies of the 2p orbitals on oxygen and fluorine, for example, decrease quite markedly when the elements are negatively charged. For oxygen ε_{2p} is 17.19e.v. but ε_{2p} is only 3.51 e.v. for the 2p orbital of O^-. Similarly the energy of a 2p orbital on fluorine is 19.86 e.v. whilst for F^-, it is 4.92 e.v. The 3d orbital of the central atom may so become on par with the energy of a ligand orbital, if the ligand has a high capacity for drawing charge off the central atom.

I feel that in view of these results, what has been termed the charge conjecture in ChapterI may indeed be the mechanism by which 3d orbitals might participate effectively in the bonding of second row elements, But before drawing all the threads together, let us look more closely at an alternative, the contraction theory.

CHAPTER VI

THE THEORY OF ORBITAL CONTRACTION

There is no absurd story that one cannot get the idlers of a great city to beleive.

Beaumarchais.

Introduction

Prior to the studies which are presented here on the 3d orbital of second row elements, only one attempt of any substance had been made to illuminate this subject. It began with the early work of Craig and Magnusson[27] and culminated in an admirable investigation of SF_6 by Craig and Zauli[28]. Their method, which will be considered in the ensuing paragraphs, yeilded the result that for the free sulphur atom, in an sp^3d^2 configuration, the 3d orbital is similar to that predicted by Slater's Rules. The 3d orbital exponent was found to be 0.61 as compared with the Slater value of 0.55. This conclusion is obtained by a calculation in which exchange items are not considered and it was thought that the inclusion of such entities would

not affect the result to any significant extent. When the present s.c.f. calculations were performed, as has been seen, the 3d orbital of $S(sp^3d^2)\ ^7F$ was found to be quite different from the Craig-Zauli 3d orbital. It seemed pertinent therefore to investigate their method more closely.

The Method of Craig and Zauli

The underlying premise of this method is that exchange phenomena produce only a slight variation in the magnitudes of the principal quantities to be evaluated, namely orbital exponents. Accordingly, the wave function ψ for $S(sp^3d^2)$ is represented by a single product of one electron functions.

$$\psi = (\phi_{1s}\cdot\phi_{2s}\cdot\phi_{2p_x}\cdot\phi_{2p_y}\cdot\phi_{2p_z})^2\cdot\phi_{3s}\cdot\phi_{3p_x}\cdot\phi_{3p_y}\cdot \cdot\phi_{3p_z}\cdot\phi_{3d_{z^2}}\cdot\phi_{3d_{x^2-y^2}}$$

Dividing the Hamiltonian H for the system into parts appropriate to the sulphur core h_c, the valence electrons h_v and the core-valence interaction V

$$H = h_c + h_v + V$$

the energy $E = \langle \psi|H|\psi \rangle$ may be written

$$E = E_{core} + I'(3s)+3I'(3p)+2I'(3d)+3J(3p) +J(3d)+3J(3s,3p)+2J(3s,3d)+6J(3p,3d)$$

where $I'(nl) = \left\langle \phi_{nl}(i) \right| -\frac{\Delta}{2} + V - \frac{16}{r_i} \left| \phi_{nl}(i) \right\rangle$

and $J(nl,nl') = \left\langle \phi^2_{nl}(i) \right| \frac{1}{r_{ij}} \left| \phi^2_{nl'}(j) \right\rangle$

It now remains but to choose a form to represent the radial portion P(r) of the functions $\phi_{nl}(i)$. In the study under discussion the 1s,2s and 2p functions,employed to generate thepotential V, are Hartree-Fock functions obtained by interpolation in tables of radial wave functions. For the valence electrons orthogonalised Slater functions are used, the core functions being replaced by single Slater functions with exponents selected to provide a maximum overlap with the Hartree-Fock functions.

$$P_{nl}(r) = \sum^{n} \lambda_{nl} . r . R_{nl}(r)$$

$$R_{nl}(r) = N_{nl} . r^{n-l} . \exp(-k_{nl} . r)$$

Finally,the values of the orbital exponents k_{3s}, k_{3p},k_{3d} which minimise the energy E are ascertained.

<u>An observation on this method</u>

Although it may prove to be trivial an idiosyncrasy in this work should not be dismissed without an assessment of its importance. Two sets of core functions are employed, s.c.f. functions and their best superimposable Slater functions.

From the viewpoint of the valence electrons,

the charge cloud presented by the core is that appropriate to the Slater functions. However the core potential V is generated from the s.c.f. functions. In the present context this is not likely to produce any marked discrepancies but the mode of the evaluation of V does raise a more serious point.

The potential V is obtained by solving Poisson's equation

$$\frac{d^2(Vr)}{dr^2} = -\frac{1}{r}\sum_{\text{all core}} P^2_{\text{core}}$$

For Hartree-Fock functions this only yields one component of the potential, in Hartree's notation, that for k = 0. This is readily to be seen from the equation for $Y_k(nl,n'l';r)$ in Chapter II page 43.

$$\frac{d^2Y_k(nl,n'l';r)}{dr^2} = \frac{k(k+1)}{r^2}\cdot Y_k(nl,n'l';r) - \frac{2k+1}{r}\cdot P(nl;r)P(n'l';r)$$

It is only for Hartree functions that terms with $k > 0$ do not occur and it is these that strictly should be employed. As but one term, $Y_2(2p,2p;r)$ is involved here there is little error. When the method is applied to heavy atoms one is likely to be less fortunate.

The core potential used by Craig and Zauli, V(CZ) with that appropriate to the Slater functions, V(S) and that for an orthogonalised 2s orbit appear

Table 11

Sulphur Core Potential (a.u.)

r	-V(CZ)	-V(S)	-V(OS)
0.010	1546.1298	1547.5021	1546.9028
0.015	1013.6286	1014.6492	1014.0829
0.020	747.8052	748.5830	748.0571
0.025	588.6532	589.2725	588.7922
0.050	272.8050	273.3252	273.0929
0.075	169.9041	170.6826	170.6594
0.100	119.8311	120.8065	120.9240
0.125	90.6027	91.6466	91.8440
0.150	71.6228	72.6361	72.8690
0.175	58.4016	59.3272	59.5666
0.200	48.7284	49.5405	49.7691
0.225	41.3943	42.0866	42.2954
0.250	35.6844	36.2607	36.4459
0.300	27.4854	27.8587	27.9967
0.400	18.2040	18.3035	18.3722
0.500	13.4254	13.3945	13.4266
0.600	10.6568	10.5846	10.5993
0.800	7.6535	7.5998	7.6029
1.000	6.0395	6.0164	6.0172
1.200	5.0108	5.0026	5.0029
1.400	4.2887	4.2861	4.2863
1.600	3.7509	3.7501	3.7502
1.800	3.3336	3.3333	3.3335
2.000	3.0001	3.0000	3.0001

in Table 11. The 2s orbit used for generating the latter potential, V(OS) is

$$P(2s) = 1.0351.r^2.\exp(-4.95r) - 0.2675.r.\exp(-15.7r)$$

Near to the nucleus a divergence between the potentials is apparent, but in the most likely neighbourhood for the valence electrons, around 2 - 3 a.u., the potential is pure coulombic. Indeed at 1 a.u. $V \simeq -6.0$ a.u. It is not surprising therefore that these variant forms of V scarcely affect the value of the integral I'(3d) in the region of the CZ minimum, $k_{3d} = 0.61$. Nor is it surprising that differences only begin to emerge as the d orbit becomes more compact. This is illustrated by Table 12 which contains I'(3d) as a function of the d orbit exponent, for the three potentials.

Table 12

Variation of I'(3d) with orbital exponent k_{3d} for different potentials V.

k_{3d}	0.6	0.7	0.8	0.9	1.0
I'(CZ)	-1.0201	-1.1552	-1.2804	-1.3957	-1.5012
I'(S)	-1.0200	-1.1551	-1.2802	-1.3955	-1.5008
I'(OS)	-1.0201	-1.1552	-1.2803	-1.3956	-1.5009

Verification of the Result of Craig and Zauli

Having ascertained that this inconsistency in Craig and Zauli's study, one may proceed to see if indeed their conclusion concerning the 3d orbit may be substantiated. The procedure adopted here consists simply in evaluating that portion of the expression for the energy E which involves the d electrons, as a function of the d orbital exponent. The 3s and 3p electrons are represented by the energy minimised functions of Craig and Zauli. These are:

$$P(3s) = 1.0917\ N_{3s}r^{3}\exp(-2.25r) - 0.4531\ N_{2s}r^{2}\exp(-4.95r) + 0.1046\ N_{1s}r\ \exp(-15.7r)$$

$$P(3p) = 1.0302\ N_{3p}r^{3}\exp(-1.91r) - 0.2478\ N_{2p}r^{2}\exp(-5.53r)$$

If the two d electrons are placed in orbits for which $m_l = 2$ and 0 respectively the energy expression, E(CZ), is obtained.

$$E(CZ) = 2I'(3d)+2F_0(3s,3d)+6F_0(3p,3d) + F_0(3d,3d)-\frac{4}{49}F_2(3d,3d)+\frac{6}{441}F_4(3d,3d)$$

For a correspondance with the s.c.f. ^7F result

$$E(^7F) = 2I'(3d)+2F_0(3s,3d)+6F_0(3p,3d) + F_0(3d,3d)-\frac{2}{49}F_2(3d,3d)-\frac{4}{441}F_4(3d,3d)$$

is appropriate. Both expressions coalesce when one considers the Hartree energy E(H), the more customary form for a calculation without exchange

$$E(H) = 2I'(3d)+2F_o(3s,3d)+6F_o(3p,3d)+F_o(3d,3d)$$

On expressing the F_k integrals in the form

$$F_k(nl,nl') = \int_o^\infty P^2(nl;r_1)dr_1 \int_o^{r_1} \frac{r_2^k}{r_1^{k+1}} \cdot P^2(nl';r_2)dr_2 + \int_o^\infty P^2(nl;r_1)dr_1 \int_{r_1}^\infty \frac{r_1^k}{r_2^{k+1}} \cdot P^2(nl';r_2)dr_2$$

as indicated in Chapter II their evaluation becomes but a nominal task. This, and all the calculation in this chapter, was programmed in Algol and performed by a KDF9 computer.

In Table I3 the various energies are given as a function of the d orbital exponent. Also appearing are $E(^7FM)$ and $E(^7FS)$; these correspond to the evaluation of $E(^7F)$ when the 3s and 3p orbits are taken to be single Slater functions with exponents given by the s.c.f. ^7F results and Slater's rules respectively. For the former $k_{3s} = 2.76$, $k_{3p} = 2.25$ and the latter $k_{3s}=k_{3p}= 2.05$.

Table 13

Variation of the Coulombic energy of Sulphur with the d orbital exponent.

k_{3d}	0.40	0.50	0.60	0.70	0.80
$F_o(dd)$	0.1033	0.1291	0.1549	0.1807	0.2065
$F_2(dd)$	0.0545	0.0681	0.0818	0.0954	0.1090
$F_4(dd)$	0.0355	0.0444	0.0533	0.0622	0.0711
$F_o(sd)$	0.1332	0.1662	0.1988	0.2308	0.2621
$F_o(pd)$	0.1332	0.1660	0.1982	0.2295	0.2597
-E(CZ)	0.2752	0.2975	0.3043	0.2978	0.2801
$-E(^7F)$	0.2737	0.2957	0.3022	0.2954	0.2773
-E(H)	0.2712	0.2926	0.2984	0.2909	0.2722
$-E(^7FM)$	0.2734	0.2934	0.2958	0.2818	0.2530
$-E(^7FS)$	0.2740	0.2954	0.3005	0.2912	0.2694

It is to be seen that all the variant forms for the energy exhibit a minimum around a value of 0.60 for k_{3d}. Craig and Zauli's result is established. More precisely E(CZ) is found to be minimised for $k_{3d} = 0.599$, $E_{min}(^7F)$ occurs at $k_{3d} = 0.596$ and $E_{min}(H)$ at $k_{3d} = 0.591$. Further, this d orbital appears to be quite unperturbed when the 3s and 3p orbitals are altered.

The Shape of the 3d Orbital

Since the time the Craig and Zauli method was proposed, it has been well established that a single exponential function provides but a primitive replica of the 3d wave function for $S(sp^3d^2)$. In order to ascertain whether their result concerning the size of the free atom orbital might be attributed to the use of such a function, Hartree's equation for the 3d orbital has been solved in a potential field appropriate to the 3p, 3s and core functions employed by Craig and Zauli.

Figure 17 illustrates the result of such a calculation. Curve A is the now familar Hartree-Fock 3d orbital for $S(sp^3d^2)$ ^7F and curve D the true Hartree orbital. These were compared in Chapter IV. The new result is represented by curve B whilst curve C is the analytic function obtained by Craig and Zauli. Curve B and D are very similar, strengthening an earlier conclusion that the shape of the 3d orbital is scarcely affected when the wave function for the other electrons are modified. Yet curve B is quite a different shape from C, although the values of $\bar{r}$ and r_{max} for the two curves are not too dissimilar. For the former $\bar{r}$

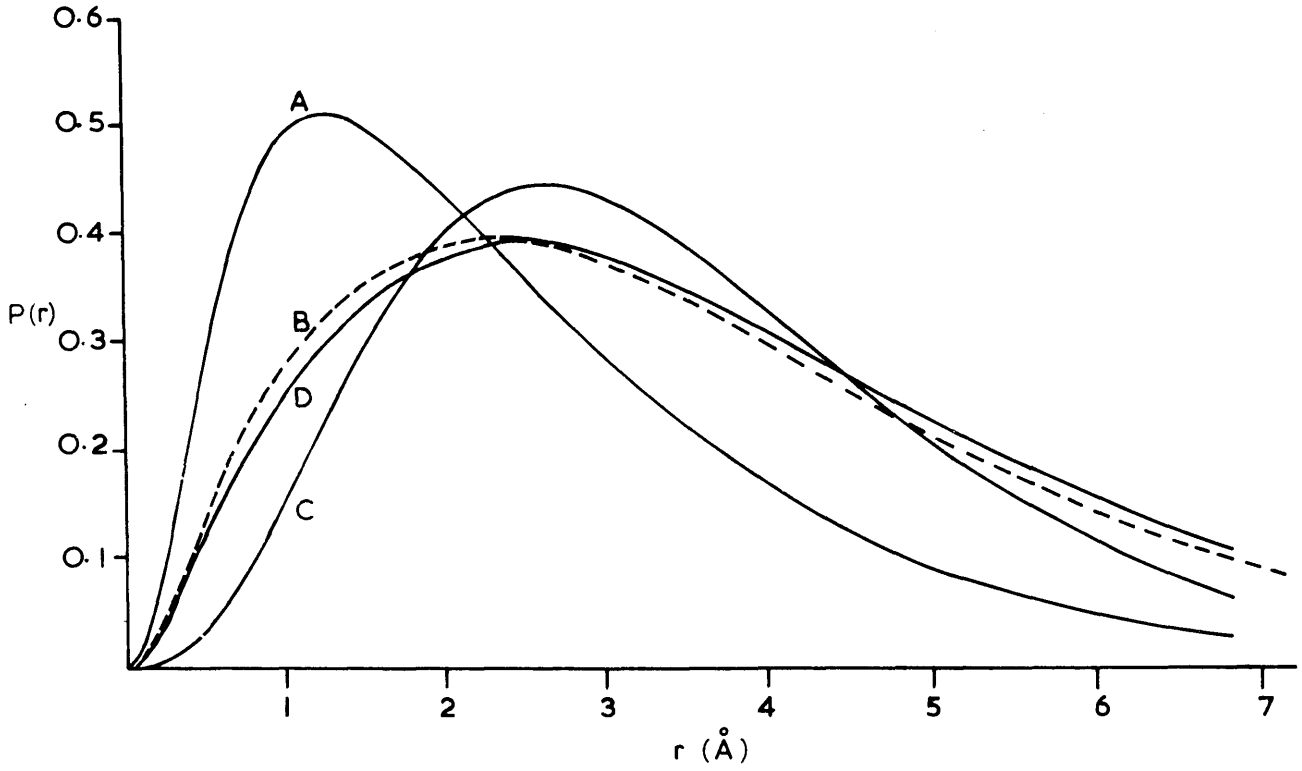


Fig. 17. Radial wave functions for the 3d orbital of $S(sp^3d^2)$: Hartree-Fock ^7F -- A, Hartree -- B; analytic orbital with exponent of 0.61 -- C; Hartree orbital when all inner orbitals are represented analytically -- D.

Table 14

Variation of $E(^7F)$ and $E(^1I)$ with d orbit exponent k_{3d} (a.u.)

k_{3d}	0.8	0.9	1.0	1.1	1.2
$-I'(3d)$	1.2804	1.3957	1.5012	1.5971	1.6833
$F_0(sd)$	0.2621	0.2923	0.3213	0.3489	0.3998
$F_0(pd)$	0.2597	0.2884	0.3156	0.3412	0.3650
$F_0(dd)$	0.2065	0.2323	0.2581	0.2840	0.3098
$F_2(dd)$	0.1090	0.1226	0.1363	0.1499	0.1635
$F_4(dd)$	0.0711	0.0800	0.0889	0.0978	0.1066
$G_2(1s,3d)$	0.0000	0.0000	0.0000	0.0000	0.0000
$G_2(2s,3d)$	0.0007	0.0014	0.0024	0.0038	0.0059
$G_1(2p,3d)$	0.0006	0.0011	0.0020	0.0033	0.0051
$G_3(2p,3d)$	0.0003	0.0007	0.0012	0.0019	0.0030
$G_2(3s,3d)$	0.0386	0.0574	0.0792	0.1029	0.1275
$G_1(3p,3d)$	0.0703	0.0997	0.1317	0.1645	0.1966
$G_3(3p,3d)$	0.0423	0.0601	0.0795	0.0995	0.1191
$-E(^7F)$	0.3859	0.4012	0.4132	0.4209	0.4231
$-E(^1I)$	0.3317	0.3321	0.3279	0.3188	0.3041

is 3.12 Å as compared with 3.04 Å, and r_{max} is 2.37 Å whilst for the Craig Zauli orbit r_{max} occurs at 2.60 Å. Curve A stands apart. Consequently in order to reconcile the Hartree-Fock result with a solution obtained by the Craig-Zauli method, as could be suspected at the outset, one needs to introduce the exchange terms.

The Influence of Exchange

According to Craig and Zauli 'on the inclusion of exchange for the 3d orbital the exponent increment is not greater than 0.03.' Viewed from the present position, this estimate, supporting their original premise, must certainly be erroneous. Table 14 confirms this statement. Here the energies of the ^7F and ^1I terms for $S(sp^3d^2)$ are tabulated as a function of the d orbital exponent. The variation of these energies with k_{3d} as compared with the energy without exchange E(H) is portrayed in Figure 18.

$$E(^7F) = 2I'(3d)+2F_o(3s,3d)+6F_o(3p,3d)+F_o(3d,3d)$$
$$-8/49\ F_2(3d,3d)-1/49\ F_4(3d,3d)-2/5\ G_2(1s,3d)$$
$$-2/5\ G_2(2s,3d)-4/5\ G_1(2p,3d)-18/35\ G_3(2p,3d)$$
$$-2/5\ G_2(3s,3d)-4/5\ G_1(3p,3d)-18/35\ G_3(3p,3d)$$

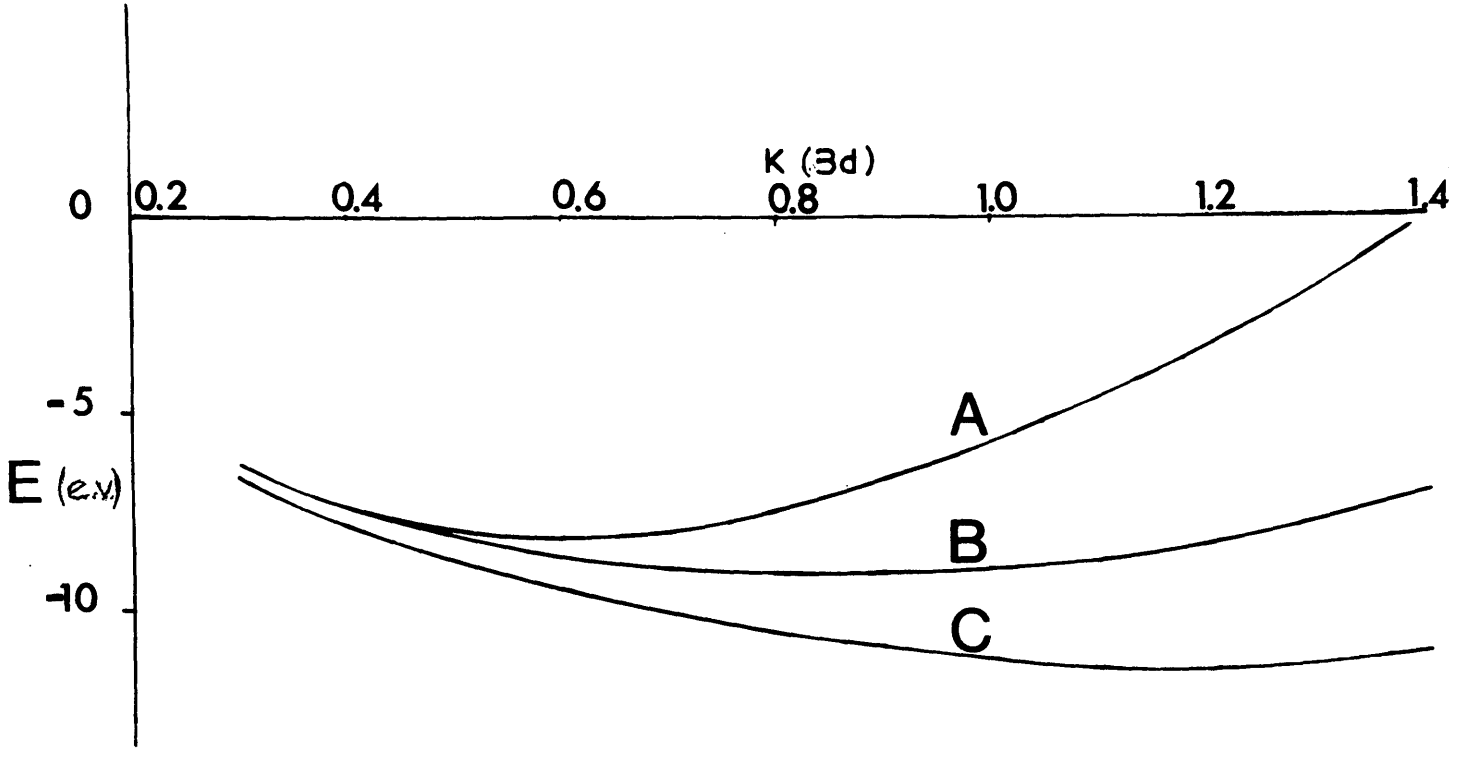


Fig. 18. The variation of the 3d electron distribution to the coulombic energy of $S(sp^3d^2)$ with orbital exponent k_{3d}.

$$E(^1I) = 2I'(3d)+2F_o(3s,3d)+6F_o(3p,3d)+F_o(3d,3d)$$
$$+4/49\ F_2(3d,3d)+1/441\ F_4(3d,3d)-2/5\ G_2(1s,3d)$$
$$-2/5\ G_2(2s,3d)-4/5\ G_1(2p,3d)-18/35\ G_3(2p,3d)$$
$$-1/5\ G_2(3s,3d)-4/5\ G_1(3p,3d)-3/35\ G_3(3p,3d)$$

The exchange integrals

$$G_k(nl,n'l') =$$
$$P(nl;r_1)P(n'l';r_1)dr_1 \frac{r_2^k}{r_1^{k+1}} \cdot P(nl;r_2)\ P(n'l';r_2)dr_2$$
$$+ P(nl;r_1)P(n'l';r_1)dr_1 \frac{r_1^k}{r_2^{k+1}} P(nl;r_2)P(n'l';r_2)dr_2$$

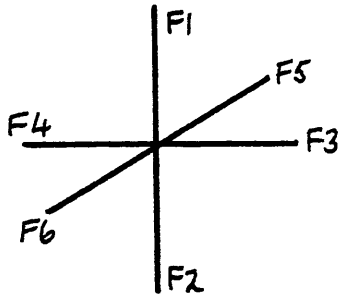
are readily computed.

It is found that the ^7F and ^1I energies are minimised for $k_{3d} = 1.18$ and 0.86 respectively. This represents an increase of 0.59 and 0.27 upon the exponent which minimises the energy without exchange E(H) and may be compared with the s.c.f. result for $S(sp^3d^2)$ ^7F which yields a single d orbital exponent of 0.98. The discrepancy between the s.c.f. result and that obtained by the Craig Zauli approach applied to the free atom is thereby resolved.

The Effect of the Ligand Field in SF_6.

Naturally when one allows for the presence of six fluorine atoms octahedrally orientated about the central sulphur atom the expression for E(CZ) acquires additional terms. These represent the interaction between the sulphur core of potential

V(S) and the fluorine nuclei of potential V(F), designated as $(S^{+};F)$, the fluorine, fluorine interactions which will vary according as the two atoms are cis $(F_1;F_3)$ or trans $(F_1;F_2)$ and the effect of the ligands upon the valence electrons. It is so possible to evaluate the coulombic energy Q of SF_6, for a variety of configurations of the central atom. Thus for $S(sp^3d^2)$



$$
\begin{aligned}
Q = {} & E_S + E_F + 12(F_1;F_3) + 3(F_1;F_2) \\
& + (3s \mid -\tfrac{\Delta}{2}^2 + V(S) \mid 3s) + 3(3p \mid -\tfrac{\Delta}{2}^2 + V(S) \mid 3p) \\
& + 2(3d \mid -\tfrac{\Delta}{2}^2 + V(S) \mid 3d) + 6(3s \mid V(F) \mid 3s) \\
& + 18(3p \mid V(F) \mid 3p) + 2(d_o \mid V(F) \mid d_o) \\
& + 4[\tfrac{1}{4}(d_o \mid V(F) \mid d_o) + \tfrac{3}{4}(d_2 \mid V(F) \mid d_2)] \\
& + 2(d_2 \mid V(F) \mid d_2) \\
& + 4[\tfrac{1}{4}(d_2 \mid V(F) \mid d_2) + \tfrac{3}{4}(d_o \mid V(F) \mid d_o)] \\
& + 3J(3p,3p) + J(3d,3d) + 3J(3s,3p) + 2J(3s,3d) \\
& + 6J(3p,3d)
\end{aligned}
$$

E_S and E_F are the energies of the sulphur core and the six ligands respectively.

One point perhaps requires elaboration. The two d electrons are considered to be in the orbitals

Table 15

Atomic and Molecular Integrals (a.u.)

$k_{3s} = 2.0$; $k_{3p} = 1.59$; $k_{3d} = 1.22$.

$(3p\ H_S\ 3p)$	2.3851	$(3p\ V(F)\ 3p)$	0.0685
$(3d\ H_s\ 3d)$	1.6994	$(3p\ V(F^-)\ 3p)$	0.2562
$J(3p,3p)$	0.3881	$(3d_o\ V(F)\ 3d_o)$	0.3005
$J(3d,3d)$	0.3029	$(3d_2\ V(F)\ 3d_2)$	0.0057
$J(3s,3p)$	0.4424	$(3d_o\ V(F^-)\ 3d_o)$	0.0536
$J(3s,3d)$	0.3719	$(3d_2\ V(F^-)\ 3d_2)$	0.2572
$J(3p,3d)$	0.3507		
$(F_1;F_3)$	0.0054	$(F_1^-;F_3)$	0.0016
$(F_1;F_2)$	0.0036	$(F_1^-;F_2)$	0.0011
$(S^{6+};F)$	0.1594	$(S^{6+};F^-)$	1.9977

$d_{x^2-y^2}$ and d_{z^2}. The interaction of F_1 and F_2 with the electron in d_z2 is $(d_o|V(F)|d_o)$. To obtain the interaction with the other four fluorines one has but to transform d_z2 into d_y2 and d_x2.

$$d_y2 = \frac{1}{2}(3y^2 - r^2)$$

$$= -\frac{1}{2} d_z2 - \frac{\sqrt{3}}{2} d_{x^2-y^2}$$

whence $(d_y2\ |V(F)|d_y2) = \frac{1}{4}(d_o|V(F)|d_o) + \frac{3}{4}(d_2|V(F)|d_2)$

Similarly the interaction of the six fluorine atoms with the electron in $d_{x^2-y^2}$ is $2(d_2|V(F)|d_2) + 4[\frac{1}{4}(d_2|V(F)|d_2) + \frac{3}{4}(d_o|V(F)|d_o)]$.

By interpolation in the tables given by Craig and Zauli, the value of all the pertinent integrals are obtained. They are listed in Table 15. For the sulphur configurations to be considered it is assumed that the valence orbitals remain unchanged and have orbital exponents of $k_{3s} = 2.0$, $k_{3p} = 1.59$ and $k_{3d} = 1.22$.

In Table 16 the energies for a number of configurations of S in SF_6 are annotated. It is interesting to observe that the popular configuration invoked for this molecule involving d orbitals, $S(sp^3d^2)$, is matched energetically by one in which there is no d orbital participation namely $S^+(s^2p^3)$.

Table 16

Energies of Configurations of SF_6

Configurations of Sulphur	$Q - E_F^o - E_S^o$ a.u. Present Evaluation	Craig and Zauli
$S(s^2p^4)$ free atom	-9.06	-9.03
$S(sp^3d^2)$	-10.19	-10.18
$S^+(sp^3d_{x^2-y^2})$	-10.05	-10.02
$S^+(sp^3d_{z^2})$	-9.96	-9.95
$S^+(s^2p^3)$	-10.20	-
$S(s^2p^4)$	-10.27	-
$S(s^2p^3d)$	-10.35	-
$S(s^2p^2d^2)$	-10.44	-

But of all the configurations noted $S(s^2p^2d^2)$ is the most favoured, being lower in energy than $S(sp^3d^2)$ by 6.80 e.v.

An ancillary feature to be observed is the large contribution to the energy which is forthcoming from the penetration integrals, involving the interaction between the d electrons and the ligands. Considering $S(sp^3d^2)$, this amounts to no less than 24.99 e.v. for each d electron.

It is not uncommon in performing semi-empirical molecular orbital calculations to disregard the penetration integrals and equate the diagonal matrix elements of the Hamiltonian α_{ii} with valence state ionisation potentials, as was mentioned in Chapter III. One may recall that for neutral species

$$\alpha_{ii} = -I_i - N_i + \frac{1}{2} J_{ii}$$

where I_i is the valence state ionisation potential, N_i the neutral atom penetration integral, and J_{ii} the coulomb repulsion between the electrons occuppying orbital i. From Table 15 it is not difficult to obtain a crude estimate of $\alpha_{3d,3d}$ in the case of $S(sp^3d^2)$ F_6. For $S(sp^3d^2)$ the orbital energy of a 3d electron is found to be + 0.75e.v. As has been demonstrated it is not strictly

permissible to identify this with an ionisation potential and in this sense the estimate of $\alpha_{3d,3d}$ is only approximate. Since the coulomb repulsion integral J(3d,3d) is 8.24 e.v., $\alpha_{3d,3d}$ is evaluated to be 20.12 e.v. Therefore to base a semi-empirical molecular orbital calculation solely on $I_{3d,3d}$ would in this instance be a dubious procedure.

In the presence of the ligand field it is to be noted that the 3d electrons of $S(sp^3d^2)$ may become energetically on par with the other valence electrons. This role for the penetration integral has been commented upon in a recent communication[92].

Conclusion

The most serious deficiency in the Craig-Zauli method is the neglect of the exchange terms. For the free atom calculations this may be overcome by incorporating an exchange potential into the theory and in pilot calculations I have obtained tolerable agreement with the results obtained by the proper procedure. For molecular calculations it is not at all clear how one should proceed, to retain the inherent simplicity of the approach and yet allow for exchange interactions in a satisfactory manner. A second flaw is the lack of orthogonality

between the valence orbitals of the central atom and the 1s orbital of the fluorine atoms. The consequence of such non-orthogonality has been demonstrated to be quite serious in a recent study of lithium hydride [93].

When all this has been said, there is no denying that this work by Craig and his collaborators has yielded some valuable insight into the manner in which d orbitals might possibly participate in the bonding of second row elements. Perhaps its most valuable contribution has been to provide a continual and significant stimulus to the subject throughout the last decade. For myself, I find the model physically unappealing but extremely tractable.

CHAPTER VII

SOME CONCLUDING REMARKS

> How are we to enrich our creative powers?
> Not by subscribing to architectural reviews,
> but by undertaking voyages of discovery
> into the inexhaustible domain of nature.
>
> Le Corbusier.

In retrospect, I feel the most significant achievement of this study has been the enlightenment of the concept of the valence state and the vanquishing of the uncertainty which had previously pervaded any discussion on the shape and energy of the 3d orbital possessed by the latter elements of the Second Row. The 3d orbital of these elements in d^1 configurations are extremely diffuse, but for d^2 and higher orbital occupation numbers they may be quite compact. For the free atom their energy is always small compared with the other valence orbitals and is a function almost solely of the state of ionisation of the atom, being independant of atomic number.

This dependance on the state of ionisation is well illustrated in Figure I where the pseudo 3d orbital energies for S, S^{+} and S^{2+} are -2 e.v., -10 e.v. and -17 e.v. respectively. The self consistent field calculations yield orbitals whose energies are just this order of magnitude as has been seen in Table 8. With regard to atomic number it might be added that the Hartree 3d orbital of oxygen $2s2p^{3}3d^{2}$ is very similar to that for a sulphur d^{2} configuration.

Although certain features of the work presented have been pursued by Craig and Thirunamachandran, the two studies do indeed complement each other. With regard to the shape of the 3d orbital the difference in approach is obvious. Here self consistent field wave functions have been calculated whilst the authors mentioned have used double exponential analytic functions to achieve their aim. When one considers the valence state of sulphur the two methods of advanee are fundamentally different. Craig and Thirunamachandran employ the techniques of valence bond theory whilst I have utilised a basic equation given originally by Dirac. He shows that for a configuration of n electrons

having a total spin S the Hamiltonian for the system may be written in the form

$$H = \sum_{P} H_p . P$$

where H_p are numerical constants and the matrices P, labelled by S, are irreducible representations of the symmetric permutation group.

When one considers the question as to the mechanism by which 3d orbitals might participate effectively in the bonding of second row elements it is very easy to ruminate. As has been seen much effort has been directed towards assessing the relative sizes of the valence orbitals of these elements, for the free atom and in a ligand field. Perhaps the first point to consider is, whether there is any need for a mechanism. My own view is that with respect to orbital size, it is probably not necessary to invoke any mechanism since the valence orbitals appear to be matched as well as is to be expected in the valence state. Though if one commences with a highly diffuse orbital it is quite natural to find, as have Craig and Zauli, that the orbital is considerably deformed by a ligand field. They have concentrated entirely on radial variations in size but it is quite likely that if one were to introduce

an angular dependance in the effective nuclear charge, the resultant orbital in a ligand field would bear little resemblance to its free atom counterpart. Craig and Zauli have also suggested that the nonexistence of SH_6 is probably due to the inability of the hydrogen atoms to produce a suitably contract 3d orbital. This conclusion seems to be at variance with Carter's study of PH_5 where a highly diffuse 3d orbital of phosphorus was found to be considerably contracted in this hypothetical molecule[94].

A mechanism for d orbital participation seems to be required when one considers the relative energies of the valence orbitals. As indicated earlier the energies of d orbitals may be considerably enhanced in SF_6 by the ligand field. Alternatively the energies of the valence and ligand orbitals might be brought on par by charge transfer. Clearly both effects are likely to be operative, and to exclude one in favour of the other would be foolhardy. The latter does provide a simple explanation for the nonexistence of SH_6 and the ability of fluorine to promulgate the second row elements under review, in high states of oxidation. For fluorine has a far greater intrinsic ability to

draw charge off the central atom of a molecule than has hydrogen, and having obtained such a negative charge is a much smaller anion.

A major obstacle in understanding the bonding of the second row elements in high oxidation states has been the gradual acceptance that a satisfactory theory may be based upon the concept of hybridisation. Indeed to change a chemists thought processes on the subject would now be extremely difficult. Nevertheless the time has now come when the hybridisation concept must be discarded if subsequent developments are not to be stifled in the manner indicated at the opening of this study.

If it may so be termed, the 3d orbital which is involved in the bonding of the elements Si, P, S, Cl or Ar is unlikely to bear any similarity to the free atom orbital. It is to be viewed in the same way as the participation of a 2p orbital of hydrogen is considered in the hydrogen molecule. This one may recall was shown in Chapter I to be grossly deformed on passing from the free atom to the molecule. The use of such a shrunken orbital, in Mulliken's terminology, is in effect to introduce

various higher excited state wave functions into the system[95].

The concept of hybridisation must now give way to the concept of polarisation.

Synopsis

The core of the studies presented here is the calculation of numerical self consistent field wave functions for the second row elements Si, P, S, Cl and Ar in excited configurations which involve the 3d orbital. In many discussions of the bonding in molecules which contain these elements asstheir central atoms,it is maintained that the 3d orbital may have an important role. To take a classic example,on the basis of the concept of hybridisation Pauling has interpreted the bonding in sulphur hexafluoride in terms of the formation by the sulphur atom of sp^3d^2 hybrids. Later it was observed that the maximum in the 3d wave function,if taken to be of a Slater type,lay well beyond the S - F internuclear distance. On further investigation, the use of the Slater 3d orbital in this context was judged to be quite acceptable and an elaborate theory was developed to bring the 3d orbital into a form suitable for bonding.

This situation persisted to the time this work was commenced,though on occasions it had been suggested that perhaps the Slater 3d orbital is not a suitable represemtation for the 3d wave

function of $S(sp^3d^2)$.

In the opening chapter of this thesis, the course of such disputations is placed in perspective against a background of the chemical thought prevailing at the period and the problems involved are formulated. For a satisfying solution it is found to be necessary to perform a series of self consistent field calculations, and to investigate more fully the concept of the valence state. Chapter II treats in detail the theory of the self consistent field and the manner in which atomic calculations are performed. This is followed by a study of the valence state concept utilising the theory of the symmetric permutation group. Some very interesting results are obtained.

The subsequent two chapters are concerned with the shape and energy of the valence orbitals possessed by the elements mentioned when in high oxidation states. It is discovered that many affirmations which have been made on the subject of the 3d orbital are unfounded and indeed quite erroneous. This is rather surprising in view of the admirable investigations performed on this topic by Craig and his collaborators during the

past decade. Their theories are therefore closely examined in Chapter VI and discrepancies explained.

On reaching the closing pages it is possible to suggest in what manner a '3d orbital' might assume a role in the bonding of the second row elements under review. Finally a plea is made that the concept of hybridisation must now give way to the concept of polarisation if the development of chemical thought is not to be inhibited.

References

[1] J.J.Berzelius Schweigger's Journal 1812 6 119.

[2] E.Frankland Phil.Trans.Roy.Soc.1852 142 417.

[3] .Wichelhaus Ann.Supp. 1868 6 257.

[4] S.Cannizzaro Il Nuovo Cimento 1858 7 321.
A.Kekule Ann. 1858 106 129.

[5] W.J.Pope,S.J.Peachy J.C.S. 1900 77 1072.

[6] S.Smiles J.C.S. 1900 77 1174.

[7] F.S.Kipping J.C.S. 1907 91 2o9,717.

[8] F.S.Kipping,F.Challenger J.C.S. 1911 99 626.

[9] De Forcrand Compt.Rend. 1905 140 764.

[10] J.J.Thomson Phil.Mag. 1904 7 237.

[11] R.Abegg. Z.Anorg.Chem 1904 39 336.

[12] W.Kossel Ann.Phys. 1916 49 229.

[13] G.N.Lewis J.A.C.S. 1916 38 762.

[14] Trans.Far.Soc. 1923 19 450.

[15] L.Pauling J.A.C.S. 1931 53 1367.

[16] L.Pauling,J.Sherman J.A.C.S. 1937 59 1450.

[17] D.F.Smith J.Chem.Phys. 1953 21 609.

[18] W.M.Tolles,W.D.Gwinn J.Chem.Phys.1962 36 1119.

[19] Interatomic Distances Ed.L.E.Sutton Chem.Soc.S.P. 11 1958.

[20] J.K.Wilmshurst,H.J.Bernstein J.Chem.Phys.1957 27 661.

[21] G.H.Duffy J.Chem.Phys.1949 17 196.
A.Golebiewski Acta Physica Polonica 1963 23 243.

[22] D.P.Craig, A.Maccoll, R.S.Nyholm, L.E.Orgel, L.E.Sutton J.C.S. 1954 332.

[23] A.Maccoll Trans Faraday Soc. 1950 46 369.

[24] F.A.Cotton J.Chem.Phys. 1961 35 228.

[25] J.C.Slater Phys.Rev. 1930 36 57.

[26] Interatomic Distances,Ed.L.E.Sutton Chem.Soc.Pub. 1958.

[27] D.P.Craig Revs.Pure App.Chem. 1954 4 4.
D.P.Craig, E.A.Magnusson J.C.S. 1956 4895.

[28] D.P.Craig, C.Zauli J.Chem.Phys.1962 37 601.

[29] L.Pauling, V.Schomaker J.A.C.S. 1939 61 1769.

[30] H.C.Longuet-Higgins Trans.Far.Soc. 1949 45 173.

[31] M.J.Bielefeld, D.Fitts J.A.C.S. 1966 88 4804.

[32] H.H.Jaffe J.Phys Chem. 1954 58 1954.

[33] G.Bergson Arkiv.fur Kemi. 1961 16 315.

[34] W.E.Moffit Proc.Roy.Soc. 1950 A200 409.

[35] D.W.J.Cruickshank J.C.S. 1961 997 5486.

[36] D.P.Craig, N.L.Paddock Nature 1958 181 1052.
D.P.Craig J.C.S. 1959 997.

[37] J.McDougal Proc.Roy.Soc. 1932 A138 550.

[38] H.Donley Phys.Rev. 1936 50 1012.

[39] S.F.Boys, V.E.Price Phil.Trans 1954 A246 451.

[40] R.E.Watson, A.J.Freeman Phys.Rev. 1961 123 521.

[41] W.R.Angus Proc.Roy.Soc 1932 A136 569.

[42] A.Syrkin, B.Belor Zhur.Fiz.Chim. 1949 23 664.

[43] R.S.Mulliken J.A.C.S. 1955 77 884.

[44] E.Clementi, D.L.Raimondi J.Chem.Phys.1963 38 2686.
G.Burns. J.Chem.Phys. 1964 41 1521.
A.Golebiewski Acta Physica Polonica 1966 29 415.

[45] F.Arndt, B.Eistert Ber. 1941 74 451.

[46] C.E.More Atomic Energy Levels; Circular No.467
National Bureau of Standards,Washington,D.C.1949.

[47] H.H.Jaffe J.Chem.Education 1956 33 25.

[48] R.E.Rundle Survey of Progress in Chemistry
1963 1 81.

[49] D.R.Hartree Proc.Camb.Phil.Soc. 1928 24 89.

[50] J.A.Gaunt Proc.Camb.Phil.Soc. 1928 24 328.

[51] J.C.Slater Phys.Rev. 1928 32 339 and 1930 35 210.

[52] P.A.M.Dirac Rroc.Roy.Soc. 1926 112 661.

[53] J.C.Slater Phys.Rev. 1929 34 1293.

[54] V.Fock Z.Physik. 1930 61 126.

[55] P.A.M.Dirac Proc.Camb.Phil.Soc. 1930 26 376.

[56] J.E.Lennard-Jones Proc.Camb.Phil.Soc.1931 27 469.

[57] D.R.Hartree The Calculation of Atomic Structures,
Wiley 1957.

[58] J.C.Slater Phys.Rev. 1951 81 385.

[59] R.Latter Phys.Rev. 1955 99 510.

[60] R.E.Watson Tech.Rept. No. 12 Solid State and
Molecular Theory Group M.I.T. 1959.

[61] E.Clementi Supplement to I.B.M. J.of Research
and Development 1965 9 2.

[62] C.C.J.Roothaan Revs.Mod.Phys. 1951 23 69.

[63] D.R.Hartree Repts.Prog.Phys. 1948 11 113.

[64] J.C.Slater Quantum Theory of Atomic Structure Volumes I and II, McGraw-Hill 1960.

[65] B.H.Worsley Proc.Roy.Soc. 1958 A247 390.

[66] C.S.Sharma, C.A.Coulson Proc.Phys.Soc.1962 80 81.

[67] C.Froese Canadian J.Phys. 1963 41 1895.

[68] E.C.Ridley Proc.Camb.Phil Soc. 1955 51 702.

[69] J.W.Cooley Math. of Comp. 1961 15 363.

[70] D.F.Mayers private communication.

[71] F.Herman, S.Skillman Atomic Structure Calculation Rrentice-Hall 1963.

[72] J.H.Van Vleck J.Chem.Phys. 1934 2 20.

[73] R.S.Mulliken J.Chem.Phys. 1934 2 789.

[74] L.Pauling Proc.Nat.Acad.Sci. 1949 35 229.

[75] C.A.Coulson lecture notes, Oxford 1961.

[76] M.Kotani Enclyopedia fur Physik.

[77] W.Moffitt Proc.Roy.Soc. 1950 A202 534.

[78] H.H.Voge J.Chem.Phys. 1936 4 581.

[79] H.Weyl The Theory of Groups and Quantum Mechanics 1928 Dover, New York.

[80] E.P.Wigner Group Theory, Academic Press 1959.

[81] R.Serber J.Chem.Phys. 1934 2 697.

[82] D.P.Craig, T.Thirunamachandran J.Chem.Phys. 1966 45 3355.

[83] W.Heitler, G.Rumer Zeit.f.Physik 1931 68 12.

[84] D.P.Craig, T.Thirunamachandran J.Chem,Phys. 1966 45 3355.

[85] D.P.Craig, T.Thirunamachandran J.Chem.Phys. 1965 43 4183.

[86] G.L.Bendazzoli, C.Zauli J.C.S. 1965 6827.

[87] J.C.Slater Phys Rev. 1932 42 33.

[88] J.W.Richardson, W.C.Nieuwpoort, R.R.Powell and W.F.Edgell J.ChemPhys. 1962 36 1057.

[89] P.C.Jordan J.Chem.Phys. 1966 44 3400, and 1964 41 1442.

[90] T.Koopmans Physica 1933 1 104.

[91] R.N.Zare J.Chem.Phys. 1966 45 1961.

[92] D.W.J.Cruickshank, B.C.Webster, M.A.Spinnler Int.J. of Quantum Chemistry Vol I in press.

[93] J.D.Stuart, R.P.Hurst Molecular Physics 1965 9 265.

[94] C.Carter Proc.Phys.Soc. 1956 69B 1297.

[95] R.S.Mulliken J.Chem.Phys. 1962 36 3428.

[96] D.W.J.Cruickshank, B.C.Webster Inorganic Sulphur Chemistry, Elseviers,in press.

Appendix I

This appendix contains the value of the integrals, F_k and G_k, occuring in the energy expressions for the multiplets quoted in the Hartree-Fock calculations. The first column of a Table indicates the orbitals concerned and the second column gives the value of k. In the third column the coefficient for the integral in the expression for the total energy is tabulated, whilst the value of the integral is listed in the fourth column. It is to be noted that when k=0 the second column is absent.

Silicon $3s^2 3p3d\ {}^3F$

F_o INTEGRALS

1s	1s	1	8.4427	1s	2s	4	2.2747
1s	2p	12	2.4161	1s	3s	4	0.6082
1s	3p	2	0.5058	1s	3d	2	0.1890
2s	2s	1	1.6116	2s	2p	12	1.6525
2s	3s	4	0.5650	2s	3p	2	0.4724
2s	3d	2	0.1889	2p	2p	15	1.7171
2p	3s	12	0.5676	2p	3p	6	0.4751
2p	3d	6	0.1889	3s	3s	1	0.4288
3s	3p	2	0.3830	3s	3d	2	0.1824
3p	3p	0	0.3492	3p	3d	1	0.1780
3d	3d	0	0.1317				

F_k INTEGRALS

2p	2p	2	1.200	0.7904	3p	3d	2	-0.057	0.0567

G_k INTEGRALS

1s	2s	0	2.000	0.1835	1s	2p	1	2.000	0.3215
1s	3s	0	2.000	0.0127	1s	3p	1	0.333	0.0159
1s	3d	2	0.200	0.0000	2s	2p	1	2.000	0.9902
2s	3s	0	2.000	0.0271	2s	3p	1	0.333	0.0191
2s	3d	2	0.200	0.0012	2p	3s	1	2.000	0.0344
2p	3p	0	1.000	0.0241	2p	3p	2	0.400	0.0234
2p	3d	1	0.400	0.0017	2p	3d	3	0.257	0.0010
3s	3p	1	0.333	0.2489	3s	3d	2	0.200	0.0315
3p	3d	1	0.400	0.0586	3p	3d	3	0.012	0.0334

Silicon $3s3p^2 3d\ {}^5F$

F_o INTEGRALS

1s	1s	1	8.4423	1s	2s	4	2.2722
1s	2p	12	2.4183	1s	3s	2	0.6142
1s	3p	4	0.5320	1s	3d	2	0.2097
2s	2s	1	1.6096	2s	2p	12	1.6524
2s	3s	2	0.5701	2s	3p	4	0.4948
2s	3d	2	0.2096	2p	2p	15	1.7192
2p	3s	6	0.5728	2p	3p	12	0.4979
2p	3d	6	0.2096	3s	3s	0	0.4341
3s	3p	2	0.3976	3s	3d	1	0.2008
3p	3p	1	0.3692	3p	3d	2	0.1964
3d	3d	0	0.1458				

F_k INTEGRALS

2p	2p	2	1.200	0.7917	3p	3p	2	0.200	0.1898
3p	3d	2	0.057	0.0658					

G_k INTEGRALS

1s	2s	0	2.000	0.1831	1s	2p	1	2.000	0.3222
1s	3s	0	1.000	0.0130	1s	3p	1	0.667	0.0176
1s	3d	2	0.200	0.0000	2s	2p	1	2.000	0.9900
2s	3s	0	1.000	0.0277	2s	3p	1	0.667	0.0211
2s	3d	2	0.200	0.0018	2p	3s	1	1.000	0.0350
2p	3p	0	2.000	0.0266	2p	3p	2	0.800	0.0260
2p	3d	1	0.400	0.0025	2p	3d	3	0.257	0.0014
3s	3p	1	0.667	0.2638	3s	3d	2	0.200	0.0405
3p	3d	1	0.400	0.0686	3p	3d	3	0.074	0.0397

Silicon $3s3p3d^2\ {}^5G$

F_o INTEGRALS

1s	1s	1	8.4426	1s	2s	4	2.2750
1s	2p	12	2.4202	1s	3s	2	0.6300
1s	3p	2	0.5816	1s	3d	4	0.2804
2s	2s	1	1.6121	2s	2p	12	1.6545
2s	3s	2	0.5841	2s	3p	2	0.5359
2s	3d	4	0.2800	2p	2p	15	1.7209
2p	3s	6	0.5869	2p	3p	6	0.5397
2p	3d	12	0.2800	3s	3s	0	0.4479
3s	3p	1	0.4238	3s	3d	2	0.2617
3p	3p	0	0.4035	3p	3d	2	0.2564
3d	3d	1	0.1993				

F_k INTEGRALS

2p	2p	2	1.200	0.7926	3d	3d	2	0.1633	0.0933
3d	3d	4	0.020	0.0583	3p	3d	2	-0.0286	0.1017

G_k INTEGRALS

1s	2s	0	2.000	0.1835	1s	2p	1	2.000	0.3227
1s	3s	0	1.000	0.0135	1s	3p	1	0.333	0.0217
1s	3d	2	0.400	0.00002	2s	2p	1	2.000	0.9913
2s	3s	0	1.000	0.0286	2s	3p	1	0.333	0.0259
2s	3d	2	0.400	0.0044	2p	3s	1	1.000	0.0365
2p	3p	0	1.000	0.0325	2p	3p	2	0.400	0.0320
2p	3d	1	0.800	0.0061	2p	3d	3	0.514	0.0034
3s	3p	1	1.000	0.2879	3s	3d	2	0.400	0.0755
3p	3d	1	0.600	0.1134	3p	3d	3	0.049	0.0668

Phosphorus $3s^2 3p^2 3d\ ^4F$

F_o INTEGRALS

1s	1s	1	9.0618	1s	2s	4	2.4796
1s	2p	12	2.6599	1s	3s	4	0.6937
1s	3p	4	0.6081	1s	3d	2	0.1815
2s	2s	1	1.7585	2s	2p	12	1.8139
2s	3s	4	0.6407	2s	3p	4	0.5625
2s	3d	2	0.1814	2p	2p	15	1.8991
2p	3s	12	0.6445	2p	3p	12	0.5669
2p	3d	6	0.1814	3s	3s	1	0.4866
3s	3p	4	0.4486	3s	3d	2	0.1762
3p	3p	1	0.4184	3p	3d	2	0.1739
3d	3d	0	0.1246				

F_k INTEGRALS

2p	2p	2	1.200	0.8783	3p	3p	2	0.200	0.2134
3p	3d	2	0.057	0.0449					

G_k INTEGRALS

1s	2s	0	2.000	0.2041	1s	2p	1	2.000	0.3673
1s	3s	0	2.000	0.0159	1s	3p	1	0.667	0.0224
1s	3d	2	0.200	0.0000	2s	2p	1	2.000	1.0824
2s	3s	0	2.000	0.0326	2s	3p	1	0.667	0.0250
2s	3d	2	0.200	0.0012	2p	3s	1	2.000	0.0412
2p	3p	0	2.000	0.0319	2p	3p	2	0.800	0.0315
2p	3d	1	0.400	0.0016	2p	3d	3	0.257	0.0009
3s	3p	1	0.667	0.2975	3s	3d	2	0.200	0.0237
3p	3d	1	0.400	0.0413	3p	3d	3	0.068	0.0236

Sulphur $3s^2 3p^4\ {}^3P$

F_o INTEGRALS

1s	1s	1	9.6810	1s	2s	4	2.6827
1s	2p	12	2.9012	1s	3s	4	0.7535
1s	3p	8	0.6473	2s	2s	1	1.9039
2s	2p	12	1.9732	2s	3s	4	0.6950
2s	3p	8	0.5995	2p	2p	15	2.0787
2p	3s	12	0.6998	2p	3p	24	0.6046
3s	3s	1	0.5254	3s	3p	8	0.4778
3p	3p	6	0.4408				

F_k INTEGRALS

2p	2p	2	1.200	0.9649	3p	3p	2	0.600	0.2202

G_k INTEGRALS

1s	2s	0	2.000	0.2244	1s	2p	1	2.000	0.4132
1s	3s	0	2.000	0.01786	1s	3p	1	1.333	0.0242
2s	2p	1	2.000	1.1726	2s	3s	0	2.000	0.0356
2s	3p	1	1.333	0.0255	2p	3s	1	2.000	0.0446
2p	3p	0	4.000	0.0329	2p	3p	2	1.600	0.0327
3s	3p	1	1.333	0.3126					

Sulphur $3s^2 3p^3 3d\ ^5D$

F_o INTEGRALS

1s 1s	1	9.6812		1s 2s	4	2.6839	
1s 2p	12	2.9023		1s 3s	4	0.7765	
1s 3p	6	0.6956		1s 3d	2	0.1805	
2s 2s	1	1.9049		2s 2p	12	1.9742	
2s 3s	4	0.7138		2s 3p	6	0.6396	
2s 3d	2	0.1803		2p 2p	15	2.0797	
2p 3s	12	0.7190		2p 3p	18	0.6456	
2p 3d	6	0.1803		3s 3s	1	0.5423	
3s 3p	6	0.5062		3s 3d	2	0.1752	
3p 3p	3	0.4765		3p 3d	3	0.1733	
3d 3d	0	0.1205					

F_k INTEGRALS

2p 2p	2	1.200	0.9656	3p 3p	2	0.600	0.2427

G_k INTEGRALS

1s 2s	0	2.000	0.2246	1s 2p	1	2.000	0.4135
1s 3s	0	2.000	0.0191	1s 3p	1	1.000	0.0283
1s 3d	2	0.200	0.0000	2s 2p	1	2.000	1.1783
2s 3s	0	2.000	0.0379	2s 3p	1	1.000	0.0297
2s 3d	2	0.200	0.0014	2p 3s	1	2.000	0.0476
2p 3p	0	3.000	0.0382	2p 3p	2	1.200	0.0382
2p 3d	1	0.400	0.0018	2p 3d	3	0.257	0.0010
3s 3p	1	1.000	0.3374	3s 3d	2	0.200	0.0215
3p 3d	1	0.400	0.0356	3p 3d	3	0.257	0.0203

Sulphur $3s3p^4 3d\ ^5F$

F_o INTEGRALS

1s	1s	1	9.6806	1s	2s	4	2.6811
1s	2p	12	2.9039	1s	3s	2	0.7862
1s	3p	8	0.6967	1s	3d	2	0.1939
2s	2s	1	1.9027	2s	2p	12	1.9736
2s	3s	2	0.7216	2s	3p	8	0.6402
2s	3d	2	0.1937	2p	2p	15	2.0813
2p	3s	6	0.7270	2p	3p	24	0.6463
2p	3d	6	0.1937	3s	3s	0	0.5498
3s	3p	4	0.5091	3s	3d	1	0.1869
3p	3p	6	0.4762	3p	3d	4	0.1842
3d	3d	0	0.1265				

F_k INTEGRALS

2p	2p	2	1.200	0.9665	3p	3p	2	0.600	0.2418
3p	3d	2	-0.057	0.0462					

G_k INTEGRALS

1s	2s	0	2.000	0.2241	1s	2p	1	2.000	0.4142
1s	3s	0	1.000	0.0197	1s	3p	1	1.333	0.0285
1s	3d	2	0.200	0.0000	2s	2p	1	2.000	1.1726
2s	3s	0	1.000	0.0391	2s	3p	1	1.333	0.0298
2s	3d	2	0.200	0.0020	2p	3s	1	1.000	0.0489
2p	3p	0	4.000	0.0383	2p	3p	2	1.600	0.0383
2p	3d	1	0.400	0.0025	2p	3d	3	0.257	0.0014
3s	3p	1	1.000	0.3379	3s	3d	2	0.200	0.0267
3p	3d	1	0.400	0.0443	3p	3d	3	0.257	0.0254

Sulphur $3s3p^3 3d^2\ {}^7F$

F_o INTEGRALS

1s	1s	1	9.6812	1s	2s	4	2.6839
1s	2p	12	2.9070	1s	3s	2	0.7912
1s	3p	6	0.7139	1s	3d	4	0.3798
2s	2s	1	1.9051	2s	2p	12	1.9761
2s	3s	2	0.7262	2s	3p	6	0.6549
2s	3d	4	0.3786	2p	2p	15	2.0841
2p	3s	6	0.7316	2p	3p	18	0.6613
2p	3d	12	0.3787	3s	3s	0	0.5541
3s	3p	3	0.5187	3s	3d	2	0.3441
3p	3p	3	0.4892	3p	3d	6	0.3336
3d	3d	1	0.2611				

F_k INTEGRALS

2p	2p	2	1.200	0.9680	3p	3p	2	0.600	0.2501
3d	3d	2	0.163	0.1173	3d	3d	4	0.020	0.0723

G_k INTEGRALS

1s	2s	0	2.000	0.2246	1s	2p	1	2.000	0.4151
1s	3s	0	1.000	0.0199	1s	3p	1	1.000	0.0299
1s	3d	2	0.400	0.0001	2s	2p	1	2.000	1.1741
2s	3s	0	1.000	0.0392	2s	3p	1	1.000	0.0312
2s	3d	2	0.400	0.0111	2p	3s	1	1.000	0.0492
2p	3p	0	3.000	0.0399	2p	3p	2	1.200	0.0401
2p	3d	1	0.800	0.0139	2p	3d	3	0.514	0.0078
3s	3p	1	1.000	0.3470	3s	3d	2	0.400	0.1125
3p	3d	1	0.800	0.1653	3p	3d	3	0.514	0.0968

Sulphur $3s3p^3 3d^2\ {}^1I$

F_o INTEGRALS

1s	1s	1	9.6813	1s	2s	4	2.6819
1s	2p	12	2.9055	1s	3s	2	0.8037
1s	3p	6	0.7078	1s	3d	4	0.3259
2s	2s	1	1.9032	2s	2p	12	1.9744
2s	3s	2	0.7345	2s	3p	6	0.6484
2s	3d	4	0.3250	2p	2p	15	2.0826
2p	3s	6	0.7403	2p	3p	18	0.6549
2p	3d	12	0.3251	3s	3s	0	0.5590
3s	3p	3	0.5160	3s	3d	2	0.3007
3p	3p	3	0.4815	3p	3d	6	0.2914
3d	3d	1	0.2171				

F_k INTEGRALS

2p	2p	2	1.200	0.9671	3p	3p	2	0.240	0.2439
3d	3d	2	-0.082	0.0941	3d	3d	4	-0.002	0.0574

G_k INTEGRALS

1s	2s	0	2.000	0.2243	1s	2p	1	2.000	0.4147
1s	3s	0	1.000	0.0211	1s	3p	1	1.000	0.0301
1s	3d	2	0.400	0.0000	2s	2p	1	2.000	1.1729
2s	3s	0	1.000	0.0417	2s	3p	1	1.000	0.0312
2s	3d	2	0.400	0.0081	2p	3s	1	1.000	0.0521
2p	3p	0	3.000	0.0401	2p	3p	2	1.200	0.0402
2p	3d	1	0.800	0.0101	2p	3d	3	0.514	0.0057
3s	3p	1	0.333	0.3411	3s	3d	2	0.200	0.0828
3p	3d	1	0.800	0.1278	3p	3d	3	0.086	0.0740